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A novel triterpene from *Ceriops tagal*

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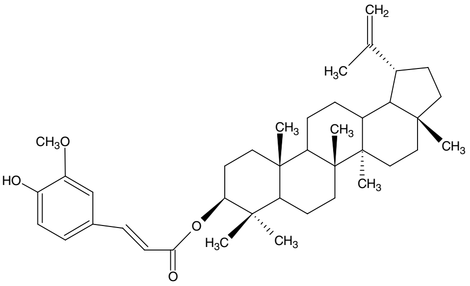
A novel lupane derivative 3β-(*E*)-feruloyllupeol has been isolated from the embryo of *Ceriops tagal*. The structure of the new triterpene was determined on the basis of spectral and chemical studies.

Ceriops tagal (Rhizophoraceae) is a species of mangrove tree distributed through Southern China, Eastern Africa and Oceania. It is used as a folk medicine in China (Lin 1984). According to primitive beliefs, the bark of *Ceriops tagal* is a powerful astringent and is used in the treatment of hemorrhage and defaecation. The oil of the species is a kind of anti-pruritic and is used in the treatment of acariasis and chilblain. The boiled water of its leaves is used as a substitute for quinine in the treatment of impaludism. Although it is such an important plant in folk medicine, the chemical constituentes of *Ceriops tagal* have not been reported. Recently ceriopsins A–G, diterpenoids from *Ceriops decandra* (syn: C. roxburghiana) of the genus *Ceriops* have been extracted (Anjaneyulu et al. 2002, 2003). We examined plant material collected from the Sanya Estuary and give the first report of the isolation of a new compound, 3β-(*E*)-feruloyllupeol (**1**) from the chloroform extract of *Ceriops tagal.*

Compound **1**, white powder from chloroform, was deduced to have the molecular formula $C_{40}H_{58}O_4$, on the basis of its FABMS, and was considered to be a triterpenoid due to a positive Liebermann-Burchard test. The IR spectrum suggested that it contained a hydroxy group (OH, 3440 cm^{-1}), a conjugated ester (C=O, 1705 cm^{-1}), an ester bond (C—O, 1170 cm^{-1}), a conjugated and trans double bond (CH=CH, 1635 and 980 cm^{-1}), a terminal double bond ($C{=}CH_2$, 3070, 1660 and 880 cm^{-1}), a geminate methyl group (1380 cm^{-1}), and a phenyl group (1600, 1580 and 1510 cm^{-1}). Its ^1H and ^{13}C NMR spectra showed great similarity to those of 3β-(*E*)-feruloybetulin and 3β-(5-hydroxyferuloy)lup-20(30)-ene (Kuo et al. 1997; Mebe et al. 1998). The ^1H NMR spectrum showed the presence of six tertiary methyl groups on saturated carbons [δ 0.80 (3 H, s), δ 1.04 (3 H, s), δ 0.88 (3 H, s), δ 0.89 (3 H, s), δ 0.95 (3 H, s), δ 0.92 (3 H, s)], which were typical of triterpene. an isopropenyl group [δ 1.69 (3 H, br s), δ 4.57 and 4.69 (each 1 H, d, J = 2.0 Hz)], an (*E*)-feruloyl moiety [δ 3.93 (3 H, s), δ 5.85 (1 H, s, –OH, disappeared on D_2O exchange), δ 6.27 and 7.58 (each 1 H, d, J = 16.0 Hz)], a deshielded methine proton on C-3 (δ 4.61, m) partially obscured by the C-30, and a typical lupenol H_β-19 proton signal (δ 2.37, m). The ^{13}C NMR spectrum showed characteristic carbon signals for the lupene moiety (Reynolds et al. 1986). The only difference was that the C-3 signal was deshielded to δ 80.9, confirming the linkage between the lupene and feruloyl moieties to be at C-3. The mass spectrum showed ions at m/z 177 (95) and 194 (13) which could be attributed to the feruloyl fragments, respectively. The ion at m/z 409 is assigned to lupeol which on loss of a hydroxyl. Thus the foregoing mass spectral evidence confirms the presence and connection at C-3 of the feruloyl and lupene moieties in compound **1**. Hydrolysis of compound **1** with 5% aqueous KOH solution yielded two products, lupeol and ferulic acid (Kuo et al. 1983, 1997; Mebe et al. 1998). Therefore the structure of compound **1** agreed with the assigned structure.

The structure of compound **1** was finally elucidated as shown, and it was named 3β-(*E*)-feruloyllupeol. Combined with HMQC, HMBC and data from literature, the spectral data were assigned.



Compound **1**

Experimental

1. Apparatus

Melting points were determined with an XT4A micro-melting point apparatus and are uncorrected. IR spectra were recorded on a Bruker 1QUI-NOX55 spectrophotometer. ^1H NMR and ^{13}H NMR spectra were recorded in $CDCl_3$ using a Bruker ARX-400 spectrometer (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR) with tetramethylsilane (TMS) as internal standard. FABMS spectra were recorded on a VG ZAB-HS spectrometer.

2. Plant material

Embryos of *Ceriops tagal* were collected from the Sanya estuary, Hannan province, China, in September 2001. The plant material was identified by Prof. You-Shao Wang, Guangdong Key Laboratory of Marine Materia Medica, South China Sea Institute of Oceanology, Chinese Academy of Sciences (CAS). A voucher specimen has been deposited in the herbarium of the South China Sea Institute of Oceaology, CAS.

3. Extraction

The air-dried and powdered embryo of *Ceriops tagal* (1.5 kg) was exhaustively extracted with 95% ethanol at room temperature three times. The ethanol solution was evaporated *in vacuo* to yield a red-brown residue (89.0 g). This residue was suspended in H_2O and defatted with petroleum ether. The aqueous layer was further extracted with chloroform and *n*-butanol successively.

4. Isolation and characterization of 1

The chloroform extract (38.6 g) was subjected to column chromatography over silica gel (100–200 mesh, 800 g, 60 × 1200 mm) using solvents of increasing polarity from petroleum ether (b.p. 60–90 °C) through acetone. In all, 120 fractions (1000 ml) were collected. The fractions showing similar spots were combined and some of the resulting combined fractions were purified by re-chromatography and crystallization. A white powder (121 mg) was obtained from frs.16–35 (petroleum : acetone, 8 : 2). Compound **1**: m.p.: 222–223 °C; IR ν_{max}^{KBr}: 3440, 3070, 1705, 1635, 1600, 1580, 1510, 1380, 1260, 1170, 980, 880 cm^{-1} H NMR (400 MHz, $CDCl_3$): 4.61 m, 2.39 m, 0.80 s, 1.04 s, 0.88 s, 0.89 s, 0.95 s, 0.92 s, 4.57d (J = 2.4) 4.69 d (J = 2.4), 1.69 s, 7.03 d, 6.90 d (J = 8.2), 7.05 dd (J = 8.2, J = 1.6), 7.57 d (J = 16.0), 6.27 d (J = 16.0), 3.92 s; ^{13}C NMR

(100 MHz, $CDCl_3$): 38.5 (C-1), 23.9 (C-2), 80.9 (C-3), 39.0 (C-4), 55.5 (C-5), 18.3 (C-6), 34.3 (C-7), 40.9 (C-8), 50.4 (C-9), 37.2 (C-10), 21.0 (C-11), 25.2 (C-12), 38.1 (C-13), 42.9 (C-14), 27.5 (C-15), 35.6 (C-16), 43.0 (C-17), 48.0 (C-18), 48.4 (C-19), 150.9 (C-20), 29.9 (C-21), 34.3 (C-22), 28.1 (C-23), 16.7 (C-24), 16.2 (C-25), 16.0 (C-26), 14.6 (C-27), 18.0 (C-28), 109.3 (C-29), 19.3 (C-30), 127.2 (C-1′), 109.4 (C-2′), 146.8 (C-3′), 147.9 (C-4′), 116.4 (C-5′), 123.0 (C-6′), 144.3 (C-7′), 114.6 (C-8′), 167.1 (C-9′), 56.0 (C−OMe); RABMS m/z (rel. int.): 602 $[M^+]$ (35), 409 (41), 194(13), 177 (95), 154 (64), 136 (55), 105 (52), 77 (100)

Hydrolysis of compound **1**: compound **1** (18 mg) was refluxed with 5% aq. KOH (10 ml) and the reaction mixture was heated at 60 °C for 8 h. The reaction mixture was diluted with H_2O (25 ml) and extracted with Et_2O. The ester extract was purified and yielded lupeol (11 mg). The aq. layer was acidified with 3% HCl and then extracted with CH_2Cl_2 giving ferulic acid (2 mg).

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Two new compounds from the seeds of *Descurainia sophia*

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Two new compounds, descurainin A (**1**) and descurainoside B (**2**), were isolated from the seeds of *Descurainia sophia* (L.) Webb ex Prantl. Their structures were elucidated by spectroscopic methods (MS, ^1H, ^{13}C and 2D NMR).

Descurainia sophia (L.) Webb ex Prantl is widely distributed in the northeast of China, and its seeds are used as a Chinese traditional medicine to relieve cough, prevent asthma, reduce edema, promote urination and have a cardiotonic effect. In some cases the seeds can also be used in the treatment of some cancers (Sun and Li 2002). In previous chemical studies, the isolation of some cardiac glycosides (Chen et al. 1981), flavonoids and phenols (Wang et al. 2004) from the seeds was reported. As our current interest in the medicinal uses of the seeds of *D. sophia*, we also carried out a phytochemical investigation on the seeds of *D. sophia*, which resulted in two new compounds, descurainin A (**1**) and descurainoside B (**2**). This paper deals with the isolation and structural elucidation of the two new constituents (Fig.) on the base of extensive studies of their MS and 1D and 2D NMR.

Compound **1** was obtained as yellow powder from methanol and responded positively to $FeCl_3$ reagent and HCl-Mg reagent which indicated that **1** belong to the flavonoids. The molecular formula of **1** was deduced as $C_{26}H_{24}O_{10}$ from the pseudomolecular ion peaks at m/z 519.3 $[M+Na]^+$ and 495.0 $[M-H]^-$ in ESI-MS and cor-

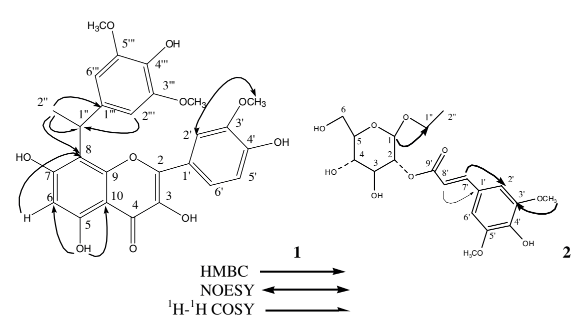

Fig.: Important correlations of compounds **1** and **2**