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A PHENOLIC AND AN ALIPHATIC LACTONE FROM *DIOSPYROS MARITIMA*

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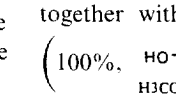
Key Word Index—*Diospyros maritima*; Ebenaceae; 3-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone; maritolide.

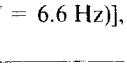
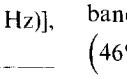
Abstract—Two new compounds, 3-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone and maritolide, have been isolated from the stem of *Diospyros maritima*. Their structures were elucidated by spectral method.

INTRODUCTION

Several reports have described the chemical constituents of some species of *Diospyros* in Taiwan including fruits of *D. discolor* Willd [1], leaves of *D. kaki* Thunb [2], bark and stem of *D. eriantha* Champ [3, 4], and stem of *D. morrisiana* Hance [5–7]. These contained triterpenes, lignans, steroids, benzoquinones, and naphthoquinones. The stems of *D. maritima* Blume (indigenous to Taiwan) is used to treat rheumatic diseases in Taiwan [8], and, therefore, their chemical constituents were of interest to us. In previous studies, we reported some new naphthoquinones [9] and triterpenes [10]. As to the naphthoquinones exhibited strong antitumour activity, we have continued our studies and isolated two new compounds from the same fraction, 3-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (**1**) and maritolide (**2**). This paper reports on the structural elucidation of these compounds.

RESULTS AND DISCUSSION

3-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (**1**) was deduced to have a molecular formula $C_{12}H_{16}O_4$ on the basis of its HREIMS. Analysis of the IR spectrum of **1** suggested that it contained a hydroxy group (3403 cm^{-1}), a conjugated ketone (1653 cm^{-1}), and an aromatic group (1586, 1507 cm^{-1}). The ^1H NMR spectrum of **1** showed the presence of an ethoxy groups [δ 1.18 (3H, *t*, J = 6.6 Hz) and 3.51 (2H, *q*, J = 6.6 Hz)], four ethylene protons [δ 3.19, and 3.83 (each 2H, *t*, J = 6.6 Hz)], a methoxy group substituted on an aromatic ring [δ 3.93 (3H, *s*)], a phenolic proton [δ 6.04 (1H, *s*, disappeared on D2O exchange)], and an ABX system of aryl protons [δ 6.92 (1H, *d*, J = 8.0 Hz), 7.52 (1H, *d*, J = 1.8 Hz), and 7.54 (1H, *dd*, J = 8.0,1.8 Hz)]. Excluding the three carbon signals (see Experimental Section) of methyl and ethoxyl groups from the 12 ^{13}C NMR signals of **1**, the remaining nine carbon signals indicated that it was a hemilignol. The presence of two neighbouring oxygenated phenyl carbon signals, one of which accounted for the UV absorption band at 276.8 nm [11], and a methoxyl group (δ 3.93) having NOESY correlation with an aryl proton signal at δ 7.52 (*d*, J = 1.8 Hz) together with a mass fragment peak at *m/z* 151 (100%, ) suggested that **1** was 3-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone. The ^{13}C NMR spectrum fully supported the assigned structure (**1**), further proof of which was obtained from NOESY and HMBC correlations (see **1**). Compound **1** was isolated as a natural product for the first time and had been synthesized without any spectral data in 1943 [12].

The HREIMS of maritolide (**2**) indicated a molecular formula $C_{14}H_{22}O_4$. IR absorption bands at 1755 and 1740 cm^{-1} suggested the presence of a $\Delta^{\alpha,\beta}$ -butenolide and an ester. The UV absorption band at 211 nm, mass fragment peaks at *m/z* 83 (46%, ) and 55 (100%, ), and three ^1H NMR signals at δ 5.01 (1H, *t*,

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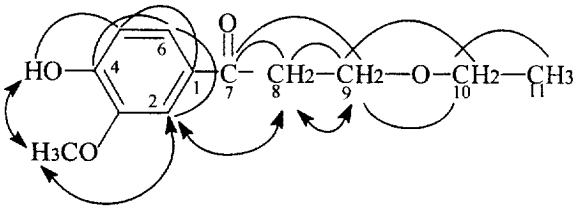
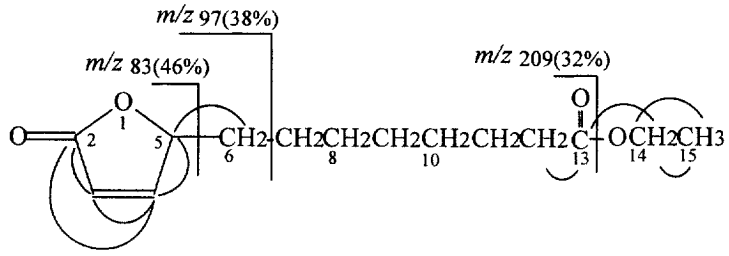


1 HMBC ——

NOESY ⟷



2 HMBC ——

J = 7.0 Hz, H-5), 6.08 and 7.41 (each 1H, *d*, J = 5.7 Hz, H-3, H-4) suggested that the presence of a 2(5*H*)-furanone moiety. The side chain was ethyl octanoate linked at C-5 of 2(5*H*)-furanone as shown by H-5 (δ 5.01, *t*). The signals at δ 4.09 (2H, *q*, J = 7.2 Hz) and 1.23 (3H, *t*, J = 7.2 Hz) were discernible as those of an ethyl ester group, and the contiguous sequence of 14 methylene protons [δ 1.31–1.62 (10H, *m*, H-7, -8, -9, -10, -11), 1.71 (2H, *m*, H-6), and 2.26 (2H, *t*, J = 7.2 Hz, H-12)] was determined by ^{1}H-^{1}H COSY. The structure **2** was fully confirmed by the ^{13}C/DEPT and HMBC. Hence, compound **2** was identified as ethyl 8-[2(5*H*)-furanon-5-yl]octanoate.

EXPERIMENTAL

General

Mp: uucorr.; ^{1}H and ^{13}C NMR: Bruker AM-300 spectrometer; EIMS, FABMS: JEOL JMS-HX 300, and JOEL JMS-HX 110, respectively; CC: silica gel (Merck 3374, 70–230 mesh).

Plant material

The stem of *Diospyros maritima* Blume were collected in Lin-Ko, Taiwan, in 1993. The plant material was identified by Mr. Muh-Tsuen Gun, formerly a technician of the Department of Botany, National Taiwan University, and a voucher specimen has been deposited at the National Research Institute of Chinese Medicine, Taipei, Taiwan, R.O.C.

Extration and isolation

The stem of *D. maritima* (16 kg) were extracted with 3 × 160 l of hot (60°) EtOH (10 hr for each extraction). The EtOH extract was evaporated *in vacuo*, yielding a black residue, which was suspended in H_2O (12 l). Then the aq soln was partitioned with *n*-hexane (1 l × 5) and *n*-BuOH (1 l × 4), successively. The combined *n*-BuOH extracts (180 g) was chromatographed on silica gel and purified by HPLC repeatedly. Two components, 3-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (**1**) (5 mg) and maritolide (**2**) (4 mg) were isolated.

3-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (**1**). Mp 72–74. UV λ_{max}^{MeOH}(log ϵ) nm: 230.0 (4.17), 276.8 (4.11), 303.2 (3.94); IR ν_{max}^{KBr} cm^{-1}: 3403 (OH), 3070, 1586, 1507 (aromatic), 1653 (conjugated C=O), 1278, 1175, 1109, 1023; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.9 (C-7), 150.4 (C-3), 146.5 (C-4), 130.0 (C-1), 123.5 (C-6), 113.8 (C-5), 109.8 (C-2), 66.0 (C-9), 66.5 (C-10), 56.0 (O*C*H3), 38.4 (C-8), 15.1 (C-11); EIMS (70 eV) *m/z* (rel. int.): 224 ([M]$^+$, 11), 180 (13), 151 (100), 123 (13); HREIMS *m/z*: 224.1048, $C_{12}H_{16}O_4$ requires 224.1049.

Maritolide (**2**). Amorphous solid, $[\alpha]_D^{24}$ − 3.4° (*c*, 0.2, $CHCl_3$); UV λ_{max}^{MeOH} (log ϵ) nm 211 (3.35); IR ν_{max}^{KBr}: cm^{-1}; 3098, 1646 (olefin), 1755, 1740, 1255, 1156, 1089 (γ-lactone, ester), 1029, 811; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 173.8 (C-2, C-13), 156.2 (C-4),

121.6 (C-3), 83.4 (C-5), 60.2 (C-14), 34.3 (C-12), 33.2 (C-6), 29.1, 29.0, 28.9, 24.9, 24.8 (C-7, -8, -9, -10, -11), 14.3 (C-15); EIMS (70 eV) *m/z* (rel. int.): 254 $[M]^+$ (1), 209 (32), 208 (40), 97 (38), 83 (46), 67 (27), 55 (100); HREIMS *m/z*: 254.1516, $C_{14}H_{22}O_4$ requires 254.1519.

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