and 177 (33) $[M-CHO]^+$. As in the case of **1**, the proposed structure for **2** was confirmed by 2D COSY experiments. Both aromatic protons were correlated to the olefinic proton at δ7.32 and only one aromatic ring proton at δ 6.63 was correlated to the OMe. Since phenylpropenoids are commonly found in most *Piper* species throughout the Caribbean and Latin America, these compounds could be considered as taxonomic markers for the genus *Piper*.

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THREE *p*-HYDROXYBENZOIC ACID DERIVATIVES FROM *TALAROMYCES DERXII*[*]

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Key Word Index—*Talaromyces derxii*; Eurotiaceae; fungus; *p*-hydroxybenzoic acid; 4-isopentenyloxybenzoic acid.

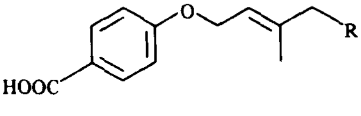
Abstract—Three new derivatives of *p*-hydroxybenzoic acid have been isolated from the culture filtrate of *Talaromyces derxii*. Their molecular structures have been investigated by spectroscopic methods.

INTRODUCTION

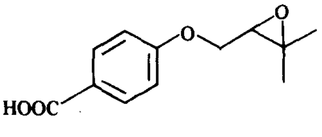
Talaromyces derxii Takada et Udagawa (anamorph: *Penicillium derxii* Takada et Udagawa), strain NHL 2982 (mating type a) is a new heterothallic fungus isolated from cultivated soil in Kurashiki, western Japan [2]. We now report the structures of three new metabolites (**1–3**) isolated from the methylene chloride extract of the culture filtrate of this fungus.

RESULTS AND DISCUSSION

The ^{1}H NMR spectrum of compound **1**, mp 150–152°, $C_{12}H_{14}O_3$, showed signals at δ 1.76 (3H), 1.81 (3H), 5.49 (1H), and 4.59 (2H) and the EI mass spectrum showed strong peaks at m/z 138 $[M-C_5H_8]^+$, 121 $[M-C_5H_9O]^+$, and 69 $[C_5H_9]^+$. These data confirmed the presence of a 3-methyl-2-butenyloxy group in the molecule of **1**. The IR spectrum of **1** (3200–2400 and 1680 cm^{-1}) showed the presence of a carboxylic acid. The ^{1}H NMR signals at δ 6.95 (2H) and 8.05 (2H) suggested the presence of a 1,4-disubstituted benzene moiety with



1 R = H
3 R = OH



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[*] Part 23 in the series 'Studies on Fungal Products'. For Part 22 see ref. [1].

an oxygen function and a carbonyl group. These results, considering the molecular formula, confirmed the structure of **1** as 4-[(3-methyl-2-butenyl)oxy]benzoic acid.

Compound **2**, mp 142–143°, $C_{12}H_{14}O_4$, had one more oxygen atom than **1**. The ^1H NMR signals of the side chain of **2** appeared at δ 1.38 (3H), 1.41 (3H), 3.16 (1H), 4.11 (1H), and 4.25 (1H). These results and the EI mass spectrum (*m/z* 138 and 121) showed that **2** was the epoxylated compound of the side chain double bond of **1**; **2** was then obtained by epoxidation of **1** with *m*-chloroperbenzoic acid. Consequently, the structure of **2** was confirmed as 4-[(2,3-epoxy-3-methylbutyl)oxy]benzoic acid.

Compound **3**, mp 140–142°, $C_{12}H_{14}O_4$, also had one more oxygen atom than **1**. The IR spectrum of **3** showed the presence of a hydroxyl group (3530 cm^{-1}) in addition to a carboxylic acid. The ^1H NMR spectrum of **3** was similar to that of **1**, except for the disappearance of one of the two methyl groups in **1** and the appearance of a signal at δ 4.03 (2H). The mass spectrum of **3** gave essentially the same fragments as those of **2**. The above results confirmed that compound **3** was the mohohydroxy derivative of **1** with the methyl group in the side chain. In order to determine the stereochemistry of the double bond, the NOE was determined. When the methylene protons at δ 4.65 in **3** were irradiated, a 12% NOE of the methyl protons at δ 1.75 was observed. Therefore, the structure of **3** was confirmed as (4*E*)-4-[4-hydroxy-3-methyl-2-butenyl)oxy]benzoic acid.

p-Hydroxybenzoic acid has already been isolated from several fungi, e.g. *Penicillium patulum* Bainier [3] and *Eurotium echinulatum* Delacroix [4], but its dimethylallyl ether (**1**) has not been isolated from any natural sources. It is interesting that compounds **2** and **3** were isolated along with **1** from the same fungus. G. Brieger reported [5] that the methyl ester of **1**, which was synthesized, had strong juvenile hormone activity against the milkweed bug.

EXPERIMENTAL

Mps: uncorr. ^1H NMR spectra (TMS int. std.) were determined at 100 MHz. Low pressure liquid chromatography (LPLC) was performed on a Chemco Low-Prep pump 81-M-2 using a glass column (200 × 10 mm) packed with silica gel CQ-3 (30–50 μ; Wako).

Isolation of metabolites. T. derxii, strain NHL 2982 (mating type a), was cultivated at 27° for 21 days in Czapek–Dox medium with 0.2% yeast ext. The culture filtrate (30 l, pH 8) was extd with CH_2Cl_2 at pH 3 and the organic layer dried (Na_2SO_4) and evapd *in vacuo*. This extract (2.7 g) was chromatographed on silica gel with $CHCl_3$ followed by purification by LPLC using C_6H_6–Me_2CO (5:1) then C_6H_6–EtOAc–HOAc (1000:100:1) to give **1** (150 mg) and **2** (12 mg), and with EtOAc–MeOH (5:1) followed by LPLC with $CHCl_3$–MeOH (5:1) to give **3** (6 mg).

4-[(*3-methyl-2-butenyl)oxy]Benzoic acid* (**1**). Leaflets (C_6H_6); mp 150–152°; UV λ_{max}^{MeOH} nm (log ε): 204 (4.34), 254 (4.25); IR ν_{max}^{KBr} cm^{-1}: 3200–2400 (COOH), 1680 (CO); (Found: C, 70.12; H, 6.90. $C_{12}H_{14}O_3$ requires: C, 69.89; H, 6.84%); ^1H NMR (100 MHz, $CDCl_3$): δ 1.76 (3H, *br s*), 1.81 (3H, *d*, $J = 0.7$ Hz), 4.59 (2H, *br d*, $J = 6.8$ Hz), 5.49 (1H, *br t*, $J = 6.8$ Hz), 6.95 (2H, *d*, $J = 8.9$ Hz), 8.05 (2H, *d*, $J = 8.9$ Hz); MS *m/z* (rel. int.): 206 $[M]^+$ (5), 138 $[M-C_5H_8]^+$ (64), 121 $[M-C_5H_9O]^+$ (20), 69 $[C_5H_9]^+$ (100).

4-[(*2,3-epoxy-3-methylbutyl)oxy]Benzoic acid* (**2**). Leaflets (C_6H_6–hexane); mp 142–143°; IR ν_{max}^{KBr} cm^{-1}: 3200–2400 (COOH), 1680 (CO); ^1H NMR (100 MHz, $CDCl_3$): δ 1.38 (3H, *s*), 1.41 (3H, *s*), 3.16 (1H, *dd*, $J = 5.4$, 4.9 Hz), 4.11 (1H, *dd*, $J = 11.0$, 5.4 Hz), 4.25 (1H, *dd*, $J = 11.0$, 4.9 Hz), 6.98 (2H, *d*, $J = 9.0$ Hz), 8.07 (2H, *d*, $J = 9.0$ Hz); MS *m/z* (rel. int.): 222 $[M]^+$ (29), 138 $[M-C_5H_8O]^+$ (75), 121 $[M-C_5H_9O_2]^+$ (65), 43 (100).

(4E)-4-[(*4-hydroxy-3-methyl-2-butenyl)oxy]Benzoic acid* (**3**). Plates (C_6H_6–EtOAc); mp 140–142°; IR ν_{max}^{KBr} cm^{-1}: 3530 (OH), 3200–2400 (COOH), 1680 (CO); ^1H NMR (100 MHz, $CDCl_3$): δ 1.75 (3H, *br s*), 4.03 (2H, *br s*), 4.65 (2H, *br d*, $J = 6.4$ Hz), 5.77 (1H, *br t*, $J = 6.4$ Hz), 6.91 (2H, *d*, $J = 8.9$ Hz), 7.98 (2H, *d*, $J = 8.9$ Hz); MS *m/z* (rel. int.): 222.0892 $[M]^+$ $[C_{12}H_{14}O_4$ requires 222.0892$]$ (3), 204.0785 $[M-H_2O]^+$ (0.8), 138.0315 $[M-C_5H_8O]^+$ (100), 121 $[M-C_5H_9O_2]^+$ (52), 84 $[C_5H_8O]^+$ (26), 43 (48).

Epoxidation of **1**. *m*-Chloroperbenzoic acid (35 mg) was added to a soln of **1** (20 mg) in CH_2Cl_2 (3 ml). After the mix. was kept overnight at room temp., the solvent was evapd *in vacuo*. The residue was purified by LPLC with C_6H_6–EtOAc–HOAc (1000:100:1) to obtain **2** (16 mg). This compound was identified with the natural metabolite mentioned above by direct comparison of TLC, ^1H NMR, IR and MS.

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