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PHENYL PROPENOIDS FROM ROOTS OF *PIPER AURITUM*

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Key Word Index—*Piper auritum*; Piperaceae; 1-propenal-3,4-(methylenedioxy)-5-methoxybenzene; 1-allyl-2,3-(methylenedioxy)-5-methoxybenzene; safrole.

Abstract—1-propenal-3,4-(methylenedioxy)-5-methoxybenzene, 1-allyl-2,3-(methylenedioxy)-5-methoxybenzene, safrole and dillapiole have been isolated from the roots of Jamaican *Piper auritum*.

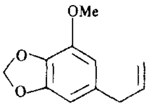
INTRODUCTION

In connection with our continuing investigation of the fruits and roots of Jamaican *Piper* species [1, 2], we have isolated four phenylpropenoids from the roots of Jamaican *Piper auritum*. Kunth. *Piper auritum*, an aromatic soft wooded shrub native to Mexico to Colombia, cultivated and escaped in Cuba, is rare in Jamaica and found on open shale road side banks and in thickets on clay soil [3]. Safrole, 1-allyl-3,4-methylenedioxybenzene is reported to be the main constituent of the essential oil from the leaves of *P. auritum* of Panama with myristicine, 1-allyl-4,5-methylenedioxy-3-methoxybenzene, as a minor component [4]. Pseudodillapiole, 1-allyl-2,3-methylenedioxy-4,5-dimethoxybenzene, was reported earlier from the Jamaican *P. aduncum* and *P. hispidum* [1]. Aporphine type alkaloids were also isolated from the roots of the Mexican variety of *P. auritum* [5]. In the present paper we describe the isolation and structure of four phenylpropenoids, compounds **1**–**4**. To our knowledge, compounds **1** and **2** have never been reported as natural products from *Piper* species.

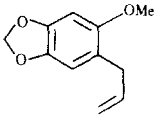
RESULTS AND DISCUSSION

Dried and milled roots of the plant (200 g) were blended with hexane. The hexane extract (4 l) upon evaporation at reduced pressure afforded a pale yellow oily residue (650 mg). Purification of this residue by silica column and TLC (hexane–Me_2CO; 4:1) yielded compounds **1** (109 mg), **2** (22 mg), **3** (62 mg) and **4** (70 mg). NMR and GC-MS analysis of compounds **3** and **4** confirmed them to be safrole, 1-allyl-3,4-methylenedioxybenzene and dillapiole, 1-allyl-4,5-methylenedioxy-2,3-dimethoxybenzene, respectively. Androstenol, cholesterol and stigmasterol were the other compounds identified by GC-MS.

Compound **1**, $C_{11}H_{12}O_3$ showed ^1H NMR ($CDCl_3$, 300 MHz) signals at 6.45 (*s*, 1H), 6.35 (*s*, 1H), 5.85 (*s*, 2H, OCH_2O), 5.80 (*m*, 1H, allylic), 5.10 (*m*, 2H, vinylic), 3.85 (*s*, 3H, OMe) and 3.30 (*d*, $J = 7$ Hz, 2H, benzylic CH_2) ppm, respectively. ^{13}C NMR ($CDCl_3$, 75 MHz) of this compound had signals at δ 148.67, 143.36, 137.24 (all aromatic carbons with oxygen) 134.50, 133.34 (olefinic), 115.78, 107.52, 102.61, 101.18 (all aromatic), 56.53 (OCH_3) and 40.28 (CH_2). The EI (mass spectrum) of compound **1** gave a $[M]^+$ at m/z 192 (100). The other important fragments were at m/z 177 (10) $[M-Me]^+$ and 161 (20) $[M-OMe]^+$. Therefore, it is evident that compound **1** is an isomer of myristicine [6]. Out of the possible six structural formulations, three structures with the *ortho* ring protons were eliminated. The proposed structure for compound **1** from the remaining three possibilities A–C was confirmed by 2D NMR spectroscopy. In the COSY spectrum it was very clear that both aromatic protons were correlated well with the OMe and only the proton at 6.35 ppm correlated to the benzylic CH_2. In myristicine (A), both aromatic protons will correlate to the CH_2 and only one to the OMe and in sarisan (B), one proton each will correlate to the CH_2 and OMe, respectively. The 2D NMR spectrum of sarisan (synthesised in this laboratory from sesamol) showed that the aromatic proton at 6.58 ppm correlated only to the CH_2 and the one at 6.42 ppm, to the OMe.



A



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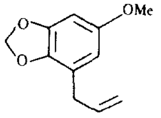
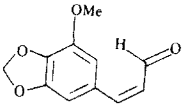


C



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Compound **2**, $C_{11}H_{10}O_4$, a colourless viscous oil, gave ^1H NMR signals at δ9.62 (*d*, $J = 8$ Hz, 1H, CHO), 7.32 (*d*, $J = 15$ Hz, 1H, Hβ to the CHO), 6.76 (*d*, $J = 1.2$ Hz, 1H), 6.63 (*d*, $J = 1.2$ Hz, 1H), 6.57 (*dd*, $J = 7$, 15 Hz, 1H, Hα to CHO), 6.10 (*s*, 2H, OCH_2O), 3.88 (*s*, 3H, OMe) and the ^{13}C NMR at δ193.36 (CHO), 152.50, 149.20, 144.00 (all aromatic carbons with oxygen attached), 128.78, 127.28 (both olefinic), 109.64, 109.58, 102.27 (all aromatic), 101.87 (methylenedioxy) and 56.80 (methoxy). Mass spectrometry of compound **2** gave a $[M]^+$ at m/z 206 (100) with other major fragments at m/z 178 (35) $[M-CO]^+$

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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.

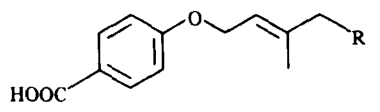
Abstract—Three new derivatives of *p*-hydroxybenzoic acid have been isolated from the culture filtrate of *Talaromyces derxii*. Their molecular structures have been investigated by spectroscopic methods.

INTRODUCTION

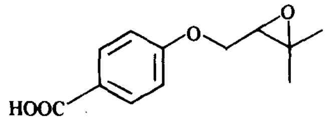
Talaromyces derxii Takada et Udagawa (anamorph: *Penicillium derxii* Takada et Udagawa), strain NHL 2982 (mating type a) is a new heterothallic fungus isolated from cultivated soil in Kurashiki, western Japan [2]. We now report the structures of three new metabolites (**1**–**3**) isolated from the methylene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