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SHORT REPORTS

TWO AMIDES FROM *PIPER AMALAGO*

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Key Word Index—*Piper amalago*; Piperaceae; alkaloids; *trans*-cinnamoylamides; 2-methoxy-4,5-methylenedioxy-*trans*-cinnamoyl piperidide; 2-methoxy-4,5-methylenedioxy-*trans*-pyrollidide.

Abstract—The hexane extracts of the roots of *Piper amalago* afforded two *trans*-cinnamoylamides, 2-methoxy-4,5-methylenedioxy-*trans*-cinnamoyl piperidide and pyrrolidide.

INTRODUCTION

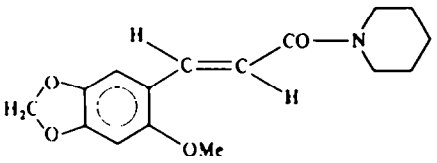
Piper species have high commercial, economical and medicinal import ice. Most are tropical herbs, but some are shrubs and trees. *Piper amalago* is distributed from Mexico to Brazil. In Mexico the Huasteco natives name it 'Kw' alaal its' (deer knee) and it is used to aleviate chest pains and as antiinflamatory [1, 2]. The chemistry of the genus *Piper* has been widely investigated, many of the compounds isolated being amides of unsaturated aryl-alkenoic acids [3–7].

RESULTS AND DISCUSSION

Hexane extracts of *P. amalago* roots afforded yellowish plates of 2-methoxy-4,5-methylenedioxy-*trans*-cinnamoyl piperidide (**1**), mp 120°, $C_{16}H_{19}O_4N$, and other yellowish crystals of 2-methoxy-4,5-methylenedioxy-*trans*-cinnamoyl pyrrolidide (**2**), mp 178–179°, $C_{15}H_{17}O_4N$. Both gave very similar ^1H NMR spectra with signals for a methylenedioxy aromatic group (δ5.95 *s*), a methoxyl (3.83 *s*), a *trans*-pair of doublets at (7.93, *d*, J = 16 Hz and 6.75, *d*, J = 16 Hz), and a pair of aromatic protons as two singlets (6.97 and 6.5). Furthermore at δ3.7 a narrow base multiplet for 4H and another at 1.6 for 6H in the spectrum of **1** and for 4H in the spectrum of **2** showed that these compounds were very closely related. The IR of both compounds exhibited amide (1693 cm^{-1}), and aromatic (1612–1587 cm^{-1}) signals confirming that both were derivatives of cinnamic acid amides.

The 14 m/z units of their mass spectra, besides the isolation of piperidine and pyrrolidine from the alkaline hydrolysis of **1** and **2** respectively, confirmed that they were *N*-[methoxy-methylenedioxy-*trans*-cinnamoyl]-piperidine and pyrrolidine amides. In their mass spectra the $[M-31]^+$ peak was base and this fragmentation has been correlated with methoxyl group contigous to the alkyl side chain of a cinnamic acid [8].

Working with material from a Guadalupe Island, W. I., Achenbach and Fietz [H. Achenbach, personal communication] have isolated other cinnamic acid amides, suggesting that maybe their plant material comes from different varieties or races than ours [9]. Already three varieties of *P. amalago* have been reported in Jamaica [10].



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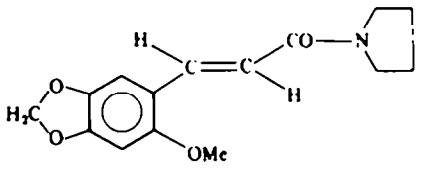

2

EXPERIMENTAL

^{1}H NMR were recorded at 60 MHz and at 350 MHz in $CDCl_3$ with TMS as int standard. MS were obtained using direct inlet at 70 eV. Elemental analysis were confirmed by HRMS. For CC silica gel was used and the "flash" technique was followed with hexane–Me_2CO in different proportions.

The plant material, was collected near Tanjajnec, S. L. P. Mexico, and identified by Dr. J. Alcorn and Prof. Dr. M. Johnston (University of Texas at Austin), a voucher specimen No. 3525 is deposited in our Herbarium. Coarsely powdered roots (4 kg) were extracted with hexane during 7 days. The hexane extracts were concd and the residues refluxed 1 hr with MeOH (1:20). The MeOH soln was concd leaving 38 g of root extracts. The extract was percolated under pressure on a silica gel column, and it was possible to isolate the following.

2-*Methxoy*-4,5-*methylenedioxy*-trans-*cinnamoyl piperidide* (1). Yellowish plates (3 g) from hexane–Me_2CO (4:1), mp 120°, $C_{16}H_{19}O_4N$, $[M]^+$ *m/z* 289. ^{1}H NMR: δ7.93 (1H, *d*, *J* = 16 Hz), 6.96 (1H, *s*), 6.75 (1H, *d*, *J* = 16 Hz), 6.5 (1H, *s*), 5.95 (3H, *s*), 3.38 (3H, *s*), 3.7 (4H, *m*), 1.6 (6H, *m*). MS *m/z* (rel. int.): 289 $[M]^+$ (15), 258 $[M-MeO]$ (100), 205 $[M-C_5H_{10}N]^+$ (80), 190 $[M-C_5H_{10}N-Me]^+$ (47), 175 $[M-C_5H_2N-2Me]^+$ (27), 162 (42), 147 (12), 119 (16), 102 (9), 91 (22), 84 (24), 63 (11). IR ν_{max}^{KBr} cm^{-1}: 3000, 2873, 1639, (CO–N), 1612 (aromatic), 1587, 1474, 1428, (C–N), 1273, 1248 (asym C–O–C), 1036, (sym. C–O–C), 1000, 980, 934 (*trans* HC=CH), 851, 758. UV λ_{max}^{EtOH} nm: 235, 285, 350.

Hydrolysis of 1. One hundred mg were refluxed 5 hr with NaOH (50 mg) in ethyleneglycol (3 ml) and H_2O (0.5 ml). After cooling and extraction with *iso* Pr ether, piperidine was identified as its picrate. The alkaline soln was acidified with 10% HCl and the yellowish ppt (19 mg) collected and purified, mp 200° decomp.

2-*Methoxy*-4,5-*methylenedioxy*-trans-*cinnamoyl pirrolidide* (2). Yellowish crystals (500 mg), mp 178°. $C_{15}H_{17}O_4N$, $[M]^+$ *m/z* 275. ^{1}H NMR: δ7.92 (1H, *d*, *J* = 16 Hz), 6.96 (1H, *s*), 6.63 (1H, *d*, *J* = 16 Hz), 6.50 (1H, *s*), 5.92 (2H, *s*), 3.78 (3H, *s*), 3.62 (*m*, 4H), 2.00 (*m*, 4H); MS *m/z* (rel. int.) 275 $[M]^+$ (11), 244 $[M-MeO]^+$ (100), 205 (69), 190 (40), 175 (20), 162 (34), 147 (10), 119 (12), 91 (14), 76 (12), 69 (12). IR ν_{max}^{KBr} cm^{-1}: 3030 (H vinylic), 2941 (CH_2 asym), 2857, 1640, (CO–N), 1587 (aromatic), 1490, 1425 (C–N, band II), 1351, 1282, 1250, 1244 (C–O–C), 1175, 1087 (C–O–C), 1015, 985 (*trans* CH=CH), 926 (methylenedioxy), 846, 761. UV λ_{max}^{EtOH} nm: 232, 282, 348.

Hydrolysis of 2. Under the same hydrolysis conditions for 1, 100 mg of 2 afforded pyrrolidine identified as its picrate. The alkaline soln afforded 28 mg of the same acid as 1 (mp, co-TLC, ^{1}H NMR, IR and mmp).

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