

A NEW BENZAMIDE FROM BARK OF AMYRIS BRENESII

CARLOS HASBUM*

Department of Chemistry, National University, Heredia 3000, Costa Rica

and OSCAR CASTRO

University of Costa Rica, School of Chemistry, CIPRONA, CONICIT Researcher, San Jose 2060, Costa Rica

The genus *Amyris* of the family Rutaceae is represented by three species in Costa Rica: *Amyris barbata* Lundell, *Amyris brenesii* Standley, and *Amyris sylvatica* Jacq. (1).

We recently reported (2) on coumarins from the bark of *A. barbata* and now describe the major components of *A. brenesii*, an additional species that accumulates mainly nitrogenated compounds. The bark of *A. brenesii* contains a small amount (0.028%) of the coumarin marmesin, identified by optical rotation, mp, uv, ir, ^1H - and ^{13}C -nmr, and ms data (3,4), and approximately 1.5% of one unusual oxazole alkaloid that was identified as *O*-(3,3-dimethylallyl)halfordinol [**1**] (mp, uv, ir, ms, and ^1H nmr compared with the literature values).

This latter compound has been isolated previously from *Aeglopsis chevalieri* Swingle (5), *Amyris plumieri* DC. (6), and *Aegle marmelos* Corr. (7), which also belong to the Rutaceae. The structural assignment of **1** was in accord with its previously unreported ^{13}C -nmr spectrum.

A new amide **2** also was isolated from *A. brenesii* and was identified as *p*-*O*-(3,3-dimethylallyl)benzamide on the basis of the following spectroscopic evidence. Ir bands at 1665, 1600, and 1420 cm^{-1} as well as a ^{13}C -nmr peak at 163.45 ppm are consistent with an aromatic amide. The ^1H nmr showed the typical signals for a 3,3-dimethylallyloxy group at δ 5.50 (t, $J = 6.6$ Hz), 4.48 (d, $J = 6.75$ Hz), 1.81 (s, Me), 1.76 (s, Me). A pair of doublets at δ 8.05 ($J = 8.6$ Hz) and

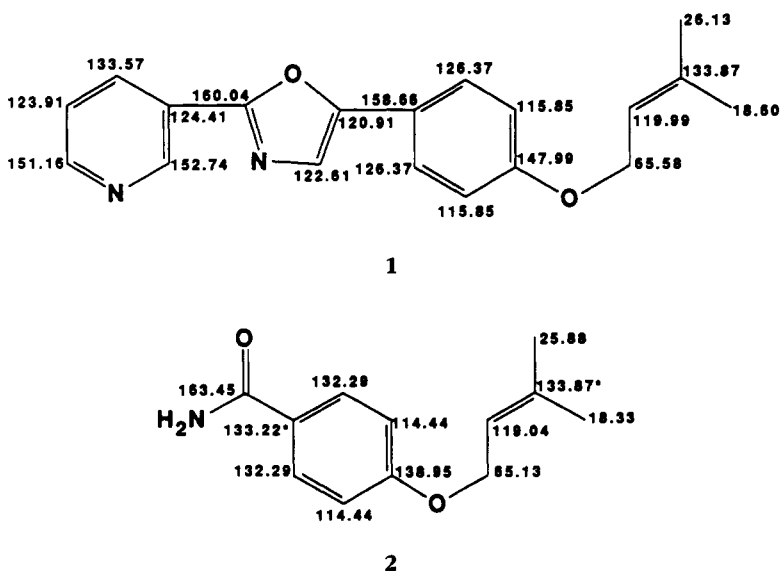


FIGURE 1. ^{13}C -nmr chemical shift assignments (ppm, CDCl_3) (Values with an asterisk may be interchanged).

6.95 ($J = 8.6$ Hz), were consistent with a 1,4-disubstituted benzene ring.

The ms spectrum of this compound provided further confirmation, because it showed the characteristic fragmentation, which produced an $[M - 69]^+$ ion and the $m/z = 69$ base peak for $[CH_2CH = C(CH_3)_2]^+$ ion. The ^{13}C -nmr chemical shift data have been summarized around **2** and were consistent with the structural assignment.

EXPERIMENTAL

PLANT MATERIAL.—*A. brevesii* was collected in Costa Rica (Rio Cuarto, Alajuela) in October 1986, and identified by L.J. Poveda A. of the Herbarium of the National Museum of Costa Rica, San Jose, where a voucher specimen (No. 118852) has been deposited.

EXTRACTION AND ISOLATION.—Powdered, dry bark (1.8 kg) was extracted exhaustively with cold MeOH by maceration. The MeOH was evaporated to yield a syrup residue from which precipitated a solid (29.9 g) consisting mainly of the oxazole alkaloid **1**. The remaining syrup was partitioned between H_2O , C_6H_{14} (55 g), and Et_2O (37.7 g).

The concentrated Et_2O extract (12 g) was fractionated by flash chromatography (600 g, Si gel 60 Merck 0.040–0.060 mm, 50-ml fractions); 70 fractions were collected using C_6H_{14} - Et_2O (1:1). Each fraction was analyzed by tlc on Si gel using $CHCl_3$ -MeOH (95:5). After successive recrystallization from C_6H_{14} - Me_2CO (2:1), fractions 12–20 afforded a new benzamide **2**.

SPECTRAL CHARACTERIZATION OF 2.—Recrystallized from $EtOAc$ - C_6H_{14} (3:1), mp 108–109°; uv λ max ($EtOH$) nm 248, 260 sh, 320; ir (KBr) ν max 2950, 2900, 2848, 1665, 1600, 1570, 1500, 1420, 1412, 1380, 1286, 1244, 1178, 1118, 990, 840, 768; 1H nmr (270 MHz, $CDCl_3$) δ 8.35 (2H, br, NH_2), 8.05 (2H, d, $J = 8.6$ Hz, H-2), 6.95 (2H, d, $J = 8.6$ Hz, H-3), 5.50 (t, $J = 6.6$ Hz, $C=CH$), 4.48 (d, $J = 6.75$ Hz, $CH_2-CH=$), 1.81 (s, Me), 1.76 (s, Me); NH_3/Cl ms m/z (%) $[M + 1]^+$ 206 (3.3), $[M + 1 - 16]^+$ 189 (3), $[M + 1 - 69]^+$ 138

(70), $[(M + 1) - 85]^+$ 121 (35); ^{13}C nmr see Figure 1.

Fractions 25–31 yielded, after Si gel chromatography, 130 mg of crude oxazole alkaloid 0-(3,3-dimethylallyl)halfordinol [**1**], which was recrystallized from a mixture of C_6H_{14} - Me_2CO (4:1) to yield 100 mg, mp 115° [mp, uv, ir, 1H nmr identical with the literature values (7)]. Loss of HCN and CO typical cleavages of 2,5-diaryloxazoles (8) from the molecular ion in the ms spectrum afforded further evidence for this structure. Fractions 42–52 yielded, after Si gel chromatography, 500 mg of the coumarin marmesin, which was recrystallized from $EtOH$, mp 182–183° [lit. (9) 181–183°] and $[\alpha]^{25} + 26.5^\circ$ [lit. (9) $[\alpha]^{25} + 26.4^\circ$].

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