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TWO NEW CHROMENILATED DIHYDROSTYRILAMIDES FROM *AMYRIS SYLVATICA*

CARLOS HASBUN,*

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

OSCAR CASTRO,

Center for the Investigation of Natural Products (CIPRONA), Department of Chemistry, University of Costa Rica, San Jose 2060, Costa Rica

and ROMANO ANDRADE

Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

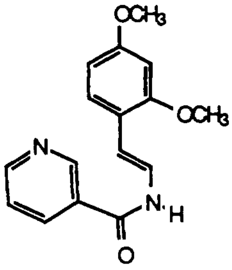
ABSTRACT.—The unusual amide *N*-(2,4-dimethoxystyryl) nicotinamide [**1**] and two new *N*-(dihydrostyryl-chromenilated) amides **2** and **3** were isolated from *Amyris sylvatica* and identified using ir, uv, hreims, ^{1}H-, and ^{13}C-nmr data.

In our earlier publications on *Amyris* species from Costa Rica we reported that *Amyris barbate* contains only coumarins (1), and that *Amyris brenessi* Standley elaborates principally the oxazole alkaloid *p*-*O*-(3,3-dimethylallyl) halfordinol and *p*-*O*-(3,3-dimethylallyl) benzamide, besides the dihydrofuranocoumarin marmesine (2).

We have isolated from *Amyris sylvatica* Jacq. (Rutaceae) the same nitrogen compounds as from *A. brenessi*, together with the unusual amide *N*-(2,4-dimethoxystyryl) nicotinamide [**1**] and two new *N*-(dihydrostyryl-chromenilated) amides **2** and **3**.

Compound **1** was identified by comparison with previously reported data (3).

Compound **2**, $C_{18}H_{25}NO_2$, mp 104–105°, was characterized on the basis of spectral data. The uv spectrum shows maxima at 265 sh and 320 nm while the ir spectrum shows absorptions suggestive of a secondary amide functionality (3300, 1640 cm^{-1}) and an aryl moiety (1545, 1485 cm^{-1}). The ^{1}H-nmr spectrum shows the presence of a trisubstituted aryl portion incorporating a chromenilated group. This was indicated by a singlet at δ 1.40 ppm integrating for six hydrogens and an AB quartet (J = 10 Hz) centered at δ 5.59 and δ 6.22 ppm. The substitution pattern on the aromatic system was revealed by the signals at δ 6.91 (dd, J = 8.5, 2 Hz), 6.78 (d, J = 2.0 Hz), and 6.69 ppm (d, J = 8.5 Hz). In addition to these, the signals at δ 2.67 (t, J = 6.5 Hz, 2H) and δ 3.45 (q, J = 6.5 Hz, 2H), the latter collapsing after D_2O exchange, and an exchangeable hydrogen at δ



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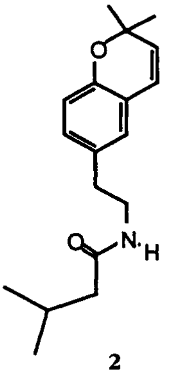
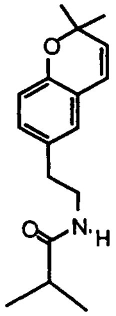


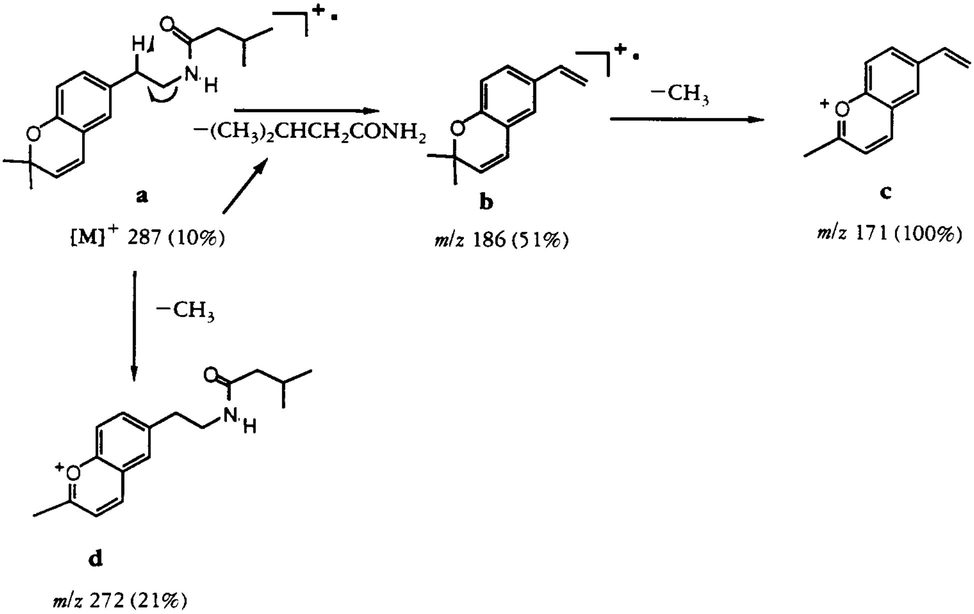
2



3

5.64 ppm were consistent with a dihydrostyrylamide group [$ArCH_2CH_2NHCO$-]. Moreover, the signals at higher field, δ 2.06 (hept, $J=7$ Hz), 1.97 (d, $J=6.5$ Hz, 2H), and 0.91 (d, $J=7$ Hz), are evidence of the presence of an isobutyl group.

In conformity with the above results, the fragments **a–d** (Scheme 1) were obtained from the high resolution mass spectral analysis of **2**.



SCHEME 1. Major mass spectral fragmentation of **2**.

The structure of amide **3** followed from a comparison of spectral data with those of amide **2**. The two compounds show ^{1}H-nmr and ^{13}C-nmr spectra that are identical with the exception of the signals due to the isopropyl group at δ 1.10 (d, $J=7$ Hz, 6H) and 2.28 (hept, $J=7$ Hz), and δ 19.5 ppm (C-3, 2Me) and 35.5 ppm (C-2). This fact, the molecular ion at *m/z* 273, and the presence of a fragment at *m/z* 259 corresponding to $[M-Me+1]^+$ in the mass spectrum, together with the same spectral fragmentation of **2**, confirm the proposed structure **3**.

EXPERIMENTAL

Uv spectra were determined in MeOH; ir spectra were determined in KBr discs; hreims was recorded on an AEI MS-50 mass spectrometer coupled to a DS-50 computer. ^{1}H-nmr and ^{13}C-nmr spectra were measured (in $CDCl_3$) on Brucker WM-360 and WH-300 spectrometers, respectively. Chemical shifts are reported in ppm (δ value from TMS). $CHCl_3$ was employed as internal standard, ^{1}H δ 7.262, ^{13}C δ 77.00 relative to TMS. Melting points are uncorrected. Further spectroscopic data is available upon request.

PLANT MATERIAL.—*A. sylvatica* was collected in Ciudad Colon, province of San Jose, in December 1984. A voucher is deposited at the herbarium of the National Museum of Costa Rica, San Jose (No. 108524) and was identified by L.J. Poveda.

ISOLATION OF CHEMICAL CONSTITUENTS.—Powdered dry roots (1.3 kg) were exhaustively extracted with cold MeOH by maceration. The solvent was evaporated to yield a syrup (58.2 g). The concentrated MeOH extract (15 g) was fractionated by flash chromatography (750 g Si gel 60 Merck 0.040–0.060 mm, 100 ml fractions) into 53 fractions using hexane-Me_2CO (3:12) as eluent. Fractions 2–7 were combined and subjected to preparative tlc on Si gel using hexane-Et_2O (1:1) which yielded *p*-*O*-(dimethylallyl) halfordinol and *p*-*O*-(dimethylallyl) benzamide (0.28 g, ^{1}H nmr, uv, ir, mp) (2). Fractions 9–28 were rechromatographed over Si gel with hexane-Me_2CO (3:1) which yielded compound **1** (0.85 g) and a mixture of **2** and **3** in the approximate proportion of 4:1 (0.4 g). Compound **1**: ^{13}C nmr ($CDCl_3$) δ 56.4, 56.4, 98.5, 104.8, 110.0, 117.5, 121.6, 123.2, 127.6, 129.7, 135.5, 147.6, 152.2, 157.4, 160.0, 162.4 ppm. Compound **2**: ^{13}C nmr δ 22.3, 26.0, 27.8, 34.8, 40.5, 46.0, 79.0, 116.2, 121.4, 122.0, 126.4, 129.1, 130.9, 131.0, 151.4, 172.4 ppm. Dried powdered leaves (946 g) were extracted and worked up as previously described, producing a greenish brown residue (30 g). This afforded *N*-(2,4-dimethoxystyryl) nicotanamide [**1**].

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