

ARISTOLODIONE, A 4,5-DIOXOAPORPHINE FROM *ARISTOLOCHIA CHILENSIS*

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The 4,5-dioxoaporphines are a small group of aporphinoids found mostly among members of the botanical families Menispermaceae, Berberidaceae, Annonaceae, Fumariaceae, and Aristolochiaceae (1). Presently, an investigation of the leaves and stems of *Aristolochia chilensis* Miers (Aristolochiaceae) supplied the known 4,5-dioxoaporphines cepharadione-A [1] (2) and 4,5-dioxodehydroasimilobine [2] (3), and the new aristolodione [3].

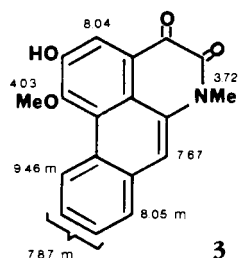
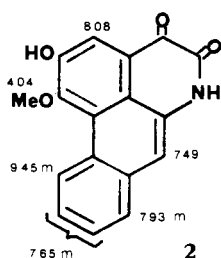
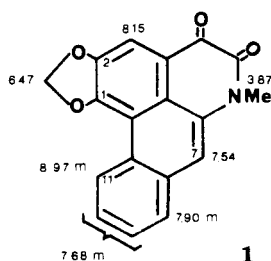
Although the ir, uv, and mass spectra of our cepharadione-A were similar to those already published for this alkaloid (2,4,5), our ¹H-nmr spectrum, obtained at 360 MHz (CDCl₃), was better defined than that previously reported (2) and has been summarized around expression 1. In particular, we were able to make specific assignments for the aromatic absorptions through the use of nmr nOe studies. Irradiation of the *N*-methyl singlet at δ 3.87 led to a 15.8% enhancement of the δ 7.54 singlet which must, therefore, be assigned to H-7. The other aromatic singlet absorption, which appears at δ 8.15, thus represents H-3.

The new phenolic alkaloid, aris-

tolodione [3], C₁₈H₁₃NO₄, was obtained as an optically inactive amorphous orange powder. The 360 MHz (DMSO-*d*₆) nmr spectrum is quoted around expression 3. An *N*-methyl singlet appears as δ 3.72; an *O*-methyl singlet is found further downfield at δ 4.03.

Again, as in the case of cepharadione-A, chemical shift assignments were confirmed by nOe studies. Irradiation of the *N*-methyl signal (δ 3.72) led to a 14.3% enhancement of H-7 (δ 7.67) so that these protons must be proximate. Additionally, irradiation of the *O*-methyl signal (δ 4.03) resulted in a 10.7% enhancement of the most downfield aromatic multiplet (δ 9.46) representing H-11. It follows that the methoxyl group is located at C-1 rather than at C-2. By the same token, the phenolic function must be bonded at the C-2 site.

With the clarification of the ¹H-nmr spectrum of aristolodione [3], the nmr spectrum of the related known alkaloid 4,5-dioxodehydroasimilobine [2] could be readily interpreted and is given around expression 2. It will be noted that in the ¹H-nmr spectra of the three alkaloids studied here, the most down-



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field aromatic absorption is due to H-11, while the most upfield aromatic signal represents H-7.

EXPERIMENTAL

PLANT COLLECTION, EXTRACTION, AND ISOLATION.—*A. chilensis* (160 g, dry leaves and stems) was collected in Lo Prado Pass, 6 miles from Santiago, Chile, in November 1985. Voucher specimens were deposited in the herbarium of the Natural History Museum in Santiago. The plant was dried, powdered, and extracted successively with petroleum ether and EtOH at room temperature. The EtOH extracts were concentrated and partitioned between CHCl_3 and 3% aqueous NaHCO_3 . The organic layer was stripped of solvent and fractionated by column chromatography over Si gel, using CHCl_3 gradually enriched with MeOH. The fractions were monitored by tlc on Si gel, using the systems CHCl_3 -MeOH (95:5) and C_6H_6 -EtOAc (3:1) and spraying with Dragendorff's reagent. Final purification of the alkaloids was on Si gel tlc glass plates using the system CHCl_3 -MeOH (95:5).

CEPHARADIONE-A [1].—Amorphous orange solid, 2 mg; uv λ max (MeOH) 234, 276, 286, 301, 313, 397, 430 nm (log ϵ 4.60, 4.39, 4.39, 4.15, 4.16, 3.96, 3.89); uv ν max (CHCl_3) 1657 cm^{-1} ; eims m/z 305 (M^+ , 54%), 277 (100), 260 (17), 248 (17), 219 (12), 163 (41), 150 (13), 138 (7).

4,5-DIOXODEHYDROASIMIOBINE [2].—

Amorphous orange solid, 2 mg. Spectrally identical with data reported in the literature (4).

ARISTOLODIONE [3].—Amorphous orange solid, 1.5 mg; uv λ max (MeOH) 239, 273, 290, 302, 314, 438 nm (log ϵ 4.70, 4.34, 4.18, 4.26, 4.28, 4.18); λ max (MeOH+OH⁻) 259, 314, 323, 395, 484 nm (log ϵ 4.59, 4.24, 4.23, 3.94, 4.01); eims m/z 307 (M^+ , 100%), 279 (62), 264 (97), 236 (50).

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