

ESCHSCHOLTZINE-N-OXIDE FROM *ESCHSCHOLTZIA CALIFORNICA*

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Eschscholtzia californica Cham. (Papaveraceae) is an annual herb introduced in Chile and widely distributed in the central zone. It is known by the names of "dedal de oro" (gold thimble) and "hierba del ferrocarril" (railway weed) (1). The petals of this species, but no other plant part, are the larval food of a great number of members of the family Noctuidae (Lepidoptera).

It is known that the plant is a rich source of isoquinoline alkaloids (2-9). Assuming that these compounds act as a chemical barrier in the plant (10) and may determine the preference of the larvae for the petals of *E. californica*, the study of the alkaloidal content of the plants was undertaken.

The dried, milled petals yielded a crude alkaloidal extract. Chromatography of the extract on a silica gel column and extensive tlc of the Dragendorff-positive fractions led to the isolation of eschscholtzine, found originally in the combined aerial parts of this plant, and another alkaloid identified as the previously undescribed eschscholtzine *N*-oxide (1).

The mass spectrum of eschscholtzine

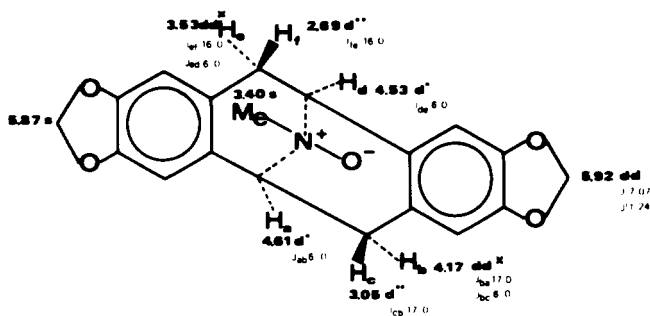
N-oxide shows a molecular ion peak at m/z 339, while the rest of the spectrum is very similar to that reported for eschscholtzine (3). The 200 MHz (CDCl₃) ¹H-nmr spectrum of this alkaloid is summarized around expression 1. Singlets at δ 6.47, 6.49, 6.58, and 6.63 ppm represent the four aromatic protons. The two methylenedioxy groups appear at δ 5.87 and 5.92 ppm, and the *N*-methyl singlet appears at δ 3.40 ppm on account of the deshielding influence of the N-O dipole, which also explains the changes in the aliphatic portion of the spectrum.

Because of the similarities of the nmr and mass spectra with those of eschscholtzine, as well as the polar nature of the compound, it was suspected that the substance isolated was eschscholtzine-*N*-oxide.

For confirmation, the compound was subjected to deoxygenation with PCl₃ affording eschscholtzine.

EXPERIMENTAL

PLANT COLLECTION, EXTRACTION AND ISOLATION.—*E. californica* (113 g, dry petals) was collected on the San Cristóbal hill in the city of Santiago, Chile, in the summer of 1984. Voucher



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Four aromatic proton singlets at δ 6.47 (1H); 6.49 (1H); 6.58 (1H); 6.63 (1H).

*Values with identical superscripts are interchangeable.

specimens have been deposited in the herbarium of the Natural History Museum in Santiago, Chile. The plant was air-dried, powdered, and extracted successively with petroleum ether and EtOH. The ethanolic extract was concentrated and partitioned between CHCl_3 and 3% aqueous citric acid. The chloroformic extract was fractionated by silica gel column chromatography using CHCl_3 gradually enriched with MeOH; the fractions were monitored by tlc on silica gel using CHCl_3 -MeOH (9:1) and spraying with Dragendorff reagent. Final purification of the Dragendorff-positive compounds was done by preparative tlc on silica gel 0.5 mm glass plates using CHCl_3 -MeOH (9:1) and CHCl_3 -EtOAc-MeOH (8:2:1) as developing systems.

(-)-*Eschscholtzine*.—Amorphous, 17 mg, identified by comparison of its physical properties and spectral data with the literature (3).

(-)-*Eschscholtzine-N-oxide* (1).—Amorphous, 23 mg; uv λ max (MeOH) 230 sh, 293 (log ϵ 3.74, 3.90); ms m/z 339 (M^+ , 5.2), 338 (3.15), 323 (31), 188 (100), 187 (37); cd Δ_ϵ (nm), 0 (296), +0.34 (283), -0.74 (240); $[\alpha]^{22}_{\text{D}}$ -213.75 (c 0.4, CHCl_3).

CONVERSION OF ESCHSCHOLTZINE-N-OXIDE TO ESCHSCHOLTZINE.—*Eschscholtzine-N-oxide* (4 mg) was dissolved in 0.5 ml CH_2Cl_2 and 0.1 ml PCl_3 was added. The mixture was stirred for 30 min at 25°. The usual work-up provided *eschscholtzine*, identified by its spectral data, and

the comparison with the base isolated from *E. californica* petals.

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