

## THALIPORPHINEMETHINE: A NEW PHENANTHRENE ALKALOID FROM *ILLIGERA PENTAPHYLLA*

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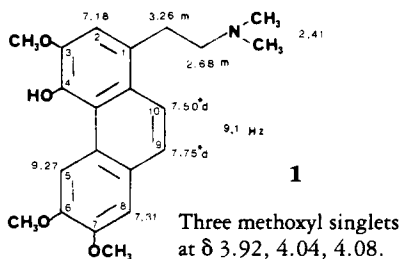
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The genus *Illigera* is one of three that make up the family Hernandiaceae, the other two being *Hernandia* and *Hazomalania*. Some thirty *Illigera* species are known from tropical Africa to Madagascar and east Asia (1). *Illigera luzonensis* (Presl.) Merr. has been partially studied and found to produce the aporphines (+)-actinodaphnine, (+)-launobine, and (+)-laurotetanine (2,3).

We have presently studied the alkaloidal content of *Illigera pentaphylla* Welw., collected in southwestern Nigeria, from which we have isolated the new amorphous phenanthrene alkaloid, thaliporphinemethine (**1**), C<sub>21</sub>H<sub>25</sub>NO<sub>4</sub>.

The <sup>1</sup>H-nmr spectrum of thaliporphinemethine in CDCl<sub>3</sub> solution at 360 MHz has been summarized in expression **1**. Three aromatic proton singlets were in evidence, including one downfield at δ 9.27 and representing H-5. Three methoxyl singlets were located at δ 3.92, 4.04, and 4.08. A hydroxyl function must be present at C-4 because a methoxyl group at that site would have adsorbed upfield in the δ 3.78-3.90 range (4). Two doublets at δ 7.50 and 7.75 due to H-9 and H-10 were also present. Finally, a dimethylamino group was denoted by a six-proton singlet at δ 2.41.

A strong uv bathochromic shift in basic solution confirmed the presence of



a phenolic function. The mass spectrum of thaliporphinemethine (**1**) exhibited a small molecular ion *m/z* 355 and a base peak *m/z* 58 due to the dimethyliminium cation.

Fourteen known alkaloids were also found, eight of which proved to be aporphines, while the remaining six were oxoaporphines. The aporphines were (+)-actinodaphnine, (+)-lindcarpine, (+)-boldine, (+)-norboldine [= (+)-laurolitsine], which is the principal alkaloid in the plant, (+)-*N*-methylindcarpine, (+)-laurotetanine, (+)-nordicentrine, and (+)-laurelliptine. The oxoaporphines were lysicamine (= oxonuciferine), oxonanthenine, oxocrebaine, dicentrinone, lanuginosine, and atheroline (4).

### EXPERIMENTAL

**PLANT COLLECTION AND EXTRACTION.**—*I. pentaphylla* (1.2 kg, dry weight) was collected near Awi, Calabar, in Cross Rivers State, in February 1982. A sample is available in the herbarium of the Forestry Research Institute of Nigeria, Eleiyele, Ibadan.

The powdered, dry plant (1 kg) was extracted with cold MeOH. The solvent was evaporated, and the residue was partitioned between 5% HCl and CHCl<sub>3</sub>. The aqueous layer was basified with

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NH<sub>4</sub>OH and extracted with CHCl<sub>3</sub> to furnish 5.5 g of crude alkaloid mixture. This material was placed on a silica gel column and eluted with CHCl<sub>3</sub>, followed by CHCl<sub>3</sub>-MeOH mixtures. Final purification was by tlc on silica gel plates in which the developing solvents were CHCl<sub>3</sub>-MeOH (95:5), CHCl<sub>3</sub>-MeOH-NH<sub>4</sub>OH (90:10:0.5), or CHCl<sub>3</sub>-MeOH-NH<sub>4</sub>OH (82:18:1). The following amounts were obtained: thaliporphinemethine (**1**) 2 mg, (+)-actinodaphnine (18 mg), (+)-lindcarpine (99 mg), (+)-boldine (20 mg), (+)-norboldine (1,675 mg), (+)-N-methylindcarpine (2 mg), (+)-laurotetanine (7 mg), (+)-nordicentrine (280 mg), (+)-laurelliptine (1 mg), lysicamine (1 mg), oxonantenine (2 mg), oxocrebanine (3 mg), dicentrinone (18 mg), lanuginosine (1 mg), and atheroline (6 mg). Known alkaloids were identified from spectral and optical data or by comparison with authentic samples.

THALIPORPHINEMETHINE (**1**).— $\lambda$  max (MeOH) 264, 276 sh, 308, 319, 346, 364, 400 nm (log  $\epsilon$  4.32, 4.05, 3.62, 3.61, 2.82, 2.66,

2.30);  $\lambda$  max (MeOH-OH<sup>-</sup>) 282 sh, 287, 309 sh nm (log  $\epsilon$  4.28, 4.29, 3.71);  $m/z$  355 (M<sup>+</sup>) (1), 297 (1), 266 (7), 58 (100).

#### ACKNOWLEDGMENTS

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