7.4 g o-dichlorobenzene, or 7.8 g o-chloro-N,N-dimethylaniline). The mixture was then heated to refluxing[6] for 1 hr after the occurrence of a color change (brown except in the case of o-bromoanisole, which was deep yellow). At this time the reaction was quenched by the portionwise addition of an excess of ammonium chloride. The amine solvent was then removed by heating with a water bath, and *ca.* 200 ml of ether was added to the residue. After the mixture was stirred for 10 min, it was filtered and the ether solution was extracted with five 50-ml portions of 10% hydrochloric acid.[7] The ether extracts containing the acid-insoluble amines were dried over anhydrous magnesium sulfate. The acid water-soluble layer was then made basic by the addition first of sodium carbonate (until the evolution of carbon dioxide ceased) and then by the addition of a few pellets of sodium hydroxide. This was followed by extraction with three 100-ml portions of ether. After the combined ether extracts were dried ($MgSO_4$) the solvent was removed by a rotary evaporator and the appropriate meta-substituted secondary aromatic amine was obtained by vacuum distillation of the residue.

Glpc analysis revealed that in all cases less than 5% of the undesired ortho isomer was obtained. This isomer, however, was easily removed by one distillation.

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(6) The mixture was heated to only 50% in the case of o-dichlorobenzene and *sec-* or isobutyl amines.

(7) No acid–base extractions were carried out in the reaction of o-chloro-N,N-dimethylaniline due to the basic mixture of the starting material or in the reaction of o-dichlorobenzene in *sec-* or isobutyl amines due to the low basicity of the corresponding m-chloro-N-alkylanilines.

The Ultraviolet Spectra of Phenolic Aporphines in Basic Solution

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Ultraviolet spectroscopy has proven a valuable tool for the structural elucidation of aporphine alkaloids. For instance, 1,2,9,10-tetrasubstituted aporphines show absorption maxima in 95% ethanol near 220, 282, and 305 mμ, while in the 1,2,10,11 series the maxima lie near 220, 270, and 305 mμ.[1-4]

In the present study, the uv spectra of a variety of monophenolic aporphines were measured in ethanol solution with a little aqueous NaOH added.[5] The presence of a phenolic function at C-9 results in a bathochromic shift which is also accompanied by a strong hyperchromic effect between 315 and 330 mμ and a minimum between 269 and 274 mμ. This is true whether the aporphine is trisubstituted as in anolobine (Figure 1) or tetrasubstituted as in actinodaphnine and N-methyllaurotetanine or even pentasubstituted as in cassyfiline (Figure 2). For comparison purposes, the uv spectral values in 95% ethanol for anolobine, actinodaphnine, N-methyllaurotetanine hydrobromide, and cassyfiline are listed in Table I.

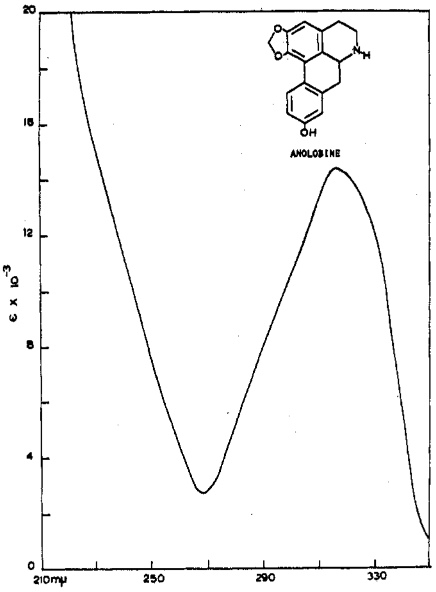

Figure 1.—Uv spectrum of anolobine in basic solution.

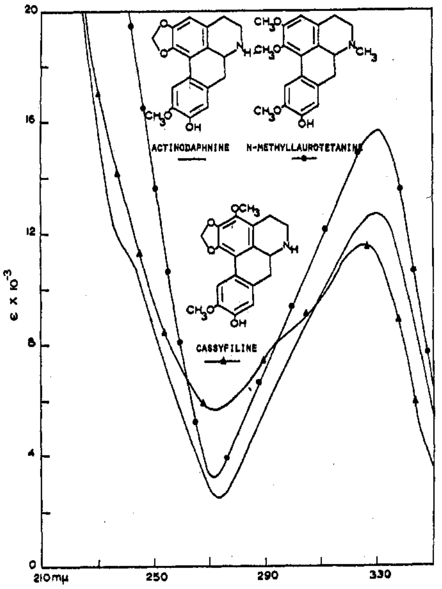

Figure 2.—Uv spectra of actinodaphnine, N-methyllaurotetanine, and cassyfiline in basic solution.

TABLE I

UV SPECTRA OF SOME APORPHINES IN 95% ETHANOL

Anolobine	λ_{max} 215, 238 sh, 280, 292 sh, and 320 mμ sh (log ε 4.21, 3.87, 4.05, 3.99, and 3.33)
Actinodaphnine	λ_{max} 219, 232 sh, 273 sh, 282, 306, and 313 mμ sh (log ε 4.17, 4.09, 3.77, 3.87, 3.92, and 3.90)
N-Methyllaurotetanine HBr	λ_{max} 219, 271 sh, 282, 303, and 313 mμ sh (log ε 4.49, 3.96, 4.06, 4.09, and 4.04)
Cassyfiline	λ_{max} 219, 240 sh, 273 sh, 283, 303, and 315 mμ sh (log ε 4.11, 3.92, 3.73, 3.84, 3.81, and 3.78)

Monophenolic aporphines such as corydine, isothebaine, N-methyl-10-methylhernovine (1,10,11-trime-

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(1) M. Shamma, *Experientia*, **16**, 484 (1960).

(2) M. Shamma and W. A. Slusarchyk, *Chem. Rev.*, **64**, 59 (1964).

(3) M. Shamma in "The Alkaloids," Vol. IX, R. H. F. Manske, Ed., Academic Press, New York, N. Y., 1967, p 1.

(4) A. W. Sangster and K. L. Stuart, *Chem. Rev.*, **65**, 69 (1965).

(5) Each spectrum was first recorded in 95% ethanol using a 1-cm standard quartz cell. The alkaloid concentration was about 16 mg/l. Two drops of aqueous 1 N NaOH solution were then added to the cell solution and the spectrum was rerun.

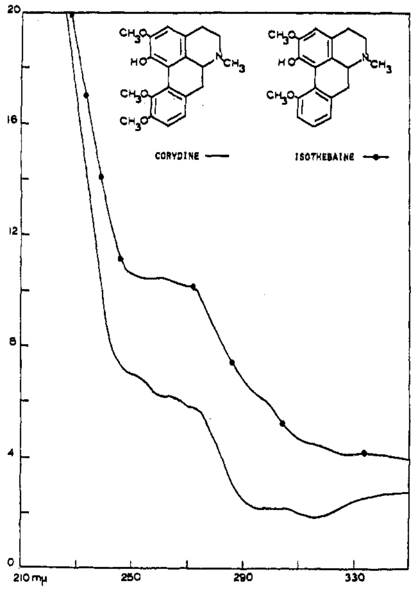

Figure 3.—Uv spectra of corydine and isothebaine in basic solution.

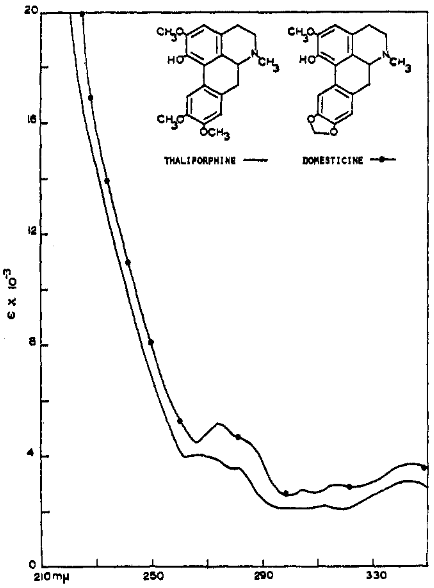

Figure 5.—Uv spectra of thaliporphine and domesticine in basic solution.

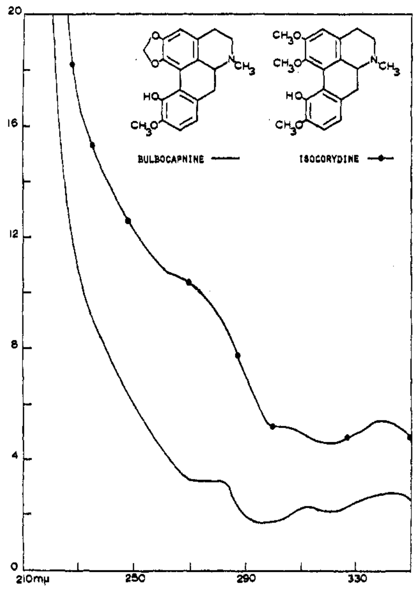

Figure 4.—Uv spectra of bulbocapnine and isocorydine in basic solution.

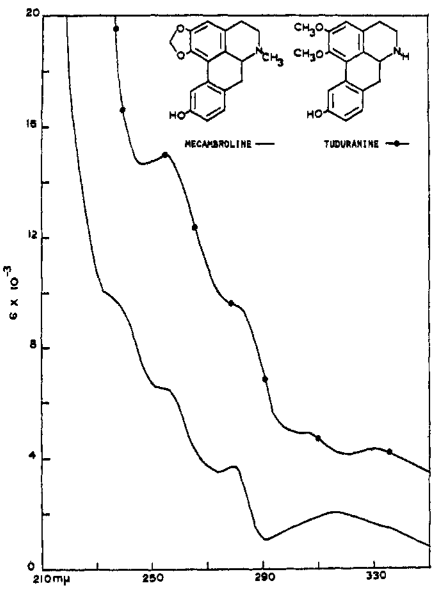

Figure 6.—Uv spectra of mecambroline and tuduranine in basic solution.

thoxy-2-hydroxyaporphine), nandigerine (1,2-methylenedioxy-10-hydroxy-11-methoxynoraporphine), bulbocapnine, isocorydine, thaliporphine, domesticine, isodomesticine (1-methoxy-2-hydroxy-9,10-methylenedioxyaporphine), mecambroline, tuduranine, phanostenine (1,2-methylenedioxy-9-methoxy-10-hydroxyaporphine), and asimilobine (1-methoxy-2-hydroxynoraporphine) which are devoid of a phenolic group at C-9 did not exhibit such a specific bathochromic and hyperchromic behavior upon the addition of base. The uv spectra in basic solution for corydine, isothebaine, bulbocapnine, isocorydine, thaliporphine, domesticine, mecambroline, and tuduranine are shown in Figures 3–6. No C-3 phenolic aporphines were available for this study. The above generalization applies only to monophenolic aporphines. If the aporphine is diphenolic, it may be converted selectively to a monophenol.[6]

Registry No.—Anolobine, 641-17-8; actinodaphnine, 517-69-1; *N*-methyllaurotetanine HBr, 26110-44-1; cassyfiline, 4030-51-7; corydine, 476-69-7; isothebaine, 568-21-8; bulbocapnine, 298-45-3; isocorydine, 475-67-2; thaliporphine, 18161-85-8; domesticine, 476-71-1; mecambroline, 3466-56-6; tuduranine, 517-97-5.

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[6] R. Tschesche, P. Welzel, and G. Legler, *Tetrahedron Lett.*, 445 (1965).