Tetrahedron Letters No.9, pp. 729-732, 1969. Pergamon Press. Printed in Great Britain.

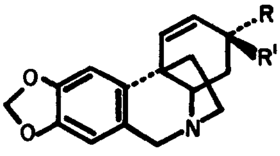
IDENTIFICATION OF AMARYLLIDACEAE ALKALOIDS UTILIZING ORD AND CD SPECTROSCOPY

G. G. DeAngelis (1) & W. C. Wildman
Iowa State University of Science and Technology
Ames, Iowa 50010

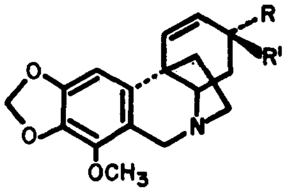
(Received in USA 12 December 1968; received in UK for publication 20 January 1969)

During the course of a recent exhaustive study of the circular dichroism (CD) and optical rotatory dispersion (ORD) behavior of the Amaryllis alkaloids, we discovered that the spectra of the different structural types of these molecules may be of diagnostic value (2).

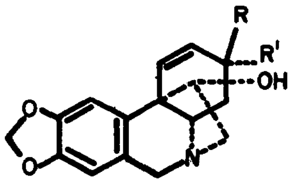
It has been found that the spectra differing in both shape and amplitude may be used as a rapid, reliable method for the identification of a new alkaloid. Utilizing the following examples we shall demonstrate that inter system identification and intra system identifications within a given structural type is possible. Various members of these ring systems are shown below.



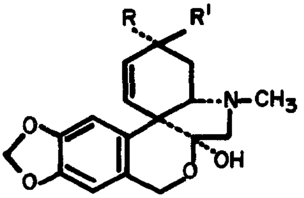
R=OH; R'=H= Crinine
R=H; R'=OH=Epicrinine



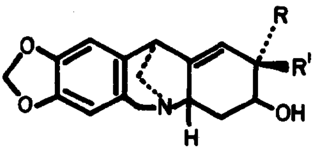
R=OH; R'=H=Powelline
R=H; R'=OH=Epipowelline



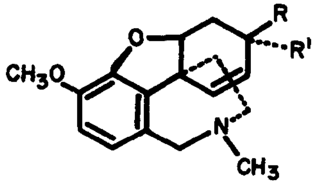
R=OCH_3; R'=H=Haemanthamine
R=H; R'=OCH_3= Crinamine
R=OH; R'=H=Alkaloid 13=(II)



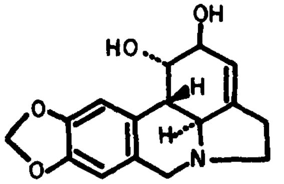
R=H; R'=OCH_3=Tazettine
R=OCH_3; R'=H=Criwelline



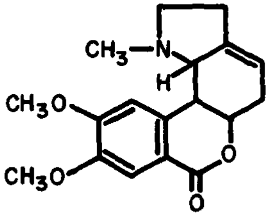
R=OCH_3; R'=H=Montanine
R=H; R'=OCH_3=Coccinine



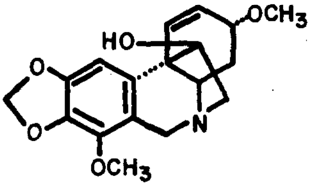
R=OH; R'=H=Galanthamine
R=H; R'=OH=Epigalanthamine



Lycorine



Homolycorine



Ambelline

Figures 1 to 3 show spectra for a representative number of compounds, and it is evident that in most cases the differences in shape and amplitude of the ORD and CD curves allow assigments to a given ring system to be made. It is clear from the general shape of the spectra

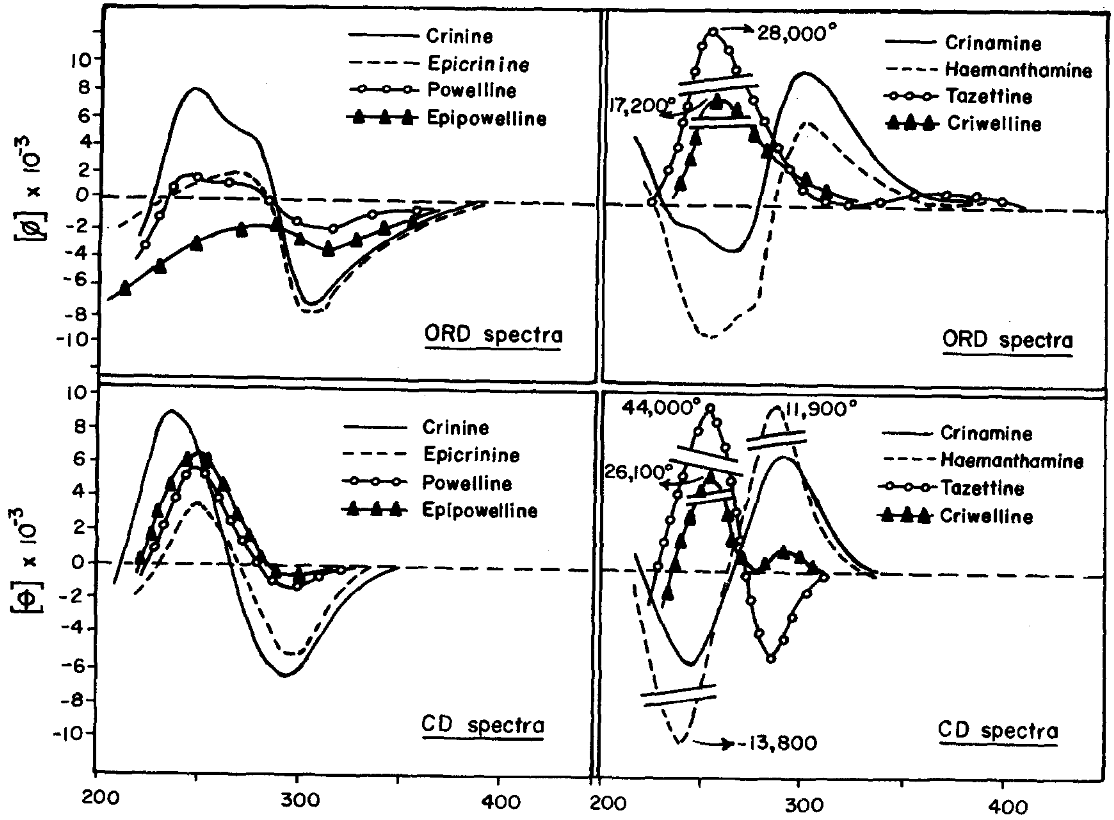


FIG. 1

that crimamine and haemanthamine are members of the same ring system but possess different stereochemistries. These alkaloids are in turn distinguishable from other ring systems.

The spectra of all of these compounds have been or will be published shortly. (6) Two examples in which the CD and ORD spectra of two alkaloids obtained in small quantity were useful in assigning each to its proper <u>ring system</u> are alkaloid (maritidine) (I) and alkaloid 13 (II) (3). The spectra are shown in figure 3, and as can be seen these can be matched in shape and intensity with the vittatine (epimer of crinine) and haemanthamine ring systems (4). The decreased amplitude of 250 mμ in the ORD of maritidine suggests that this compound may have the α-configuration at C_3.

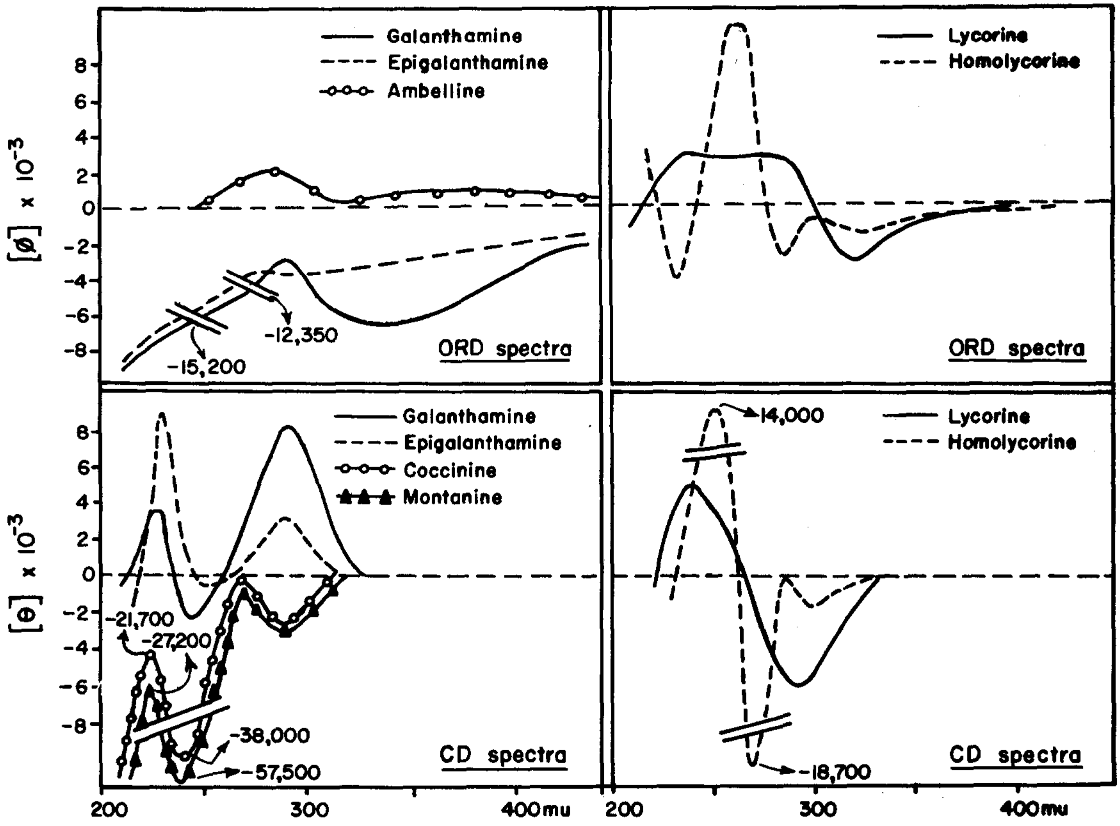


FIG. 2

The difference in overall amplitude between vittatine and **maritidine may be due** to the dimethoxy vs the methylenedioxy group, the latter causing more strain in the benzene ring which gives rise to higher ellipticities (5).

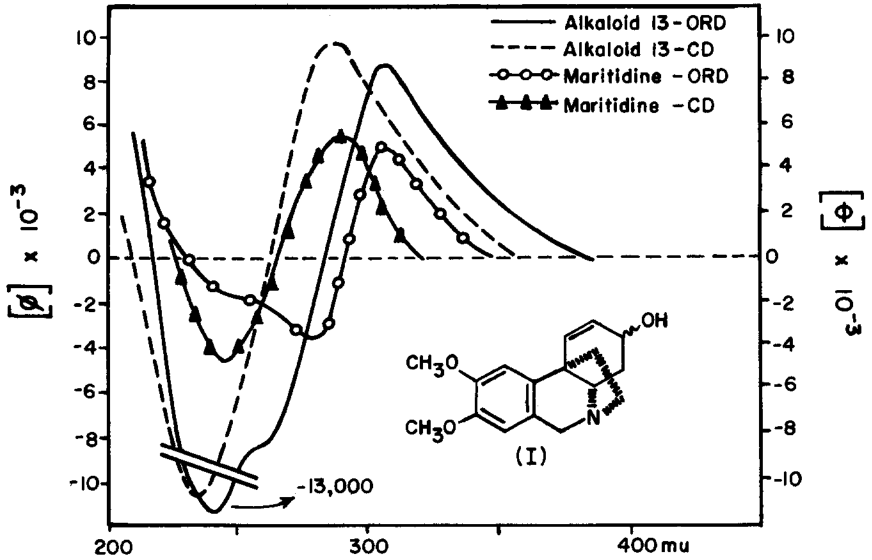


FIG. 3

1. Present Address, Chas. Pfizer & Co., Groton, Conn. 06340

2. G. G. DeAngelis, Dichroism and Dispersion Studies of the Optically Active Aromatic Chromophore, Ph.D. Thesis, Ames, Iowa, Library, Iowa State University (1966).

3. Personal Communication, **C. H. Michel,** Iowa State University, Ames, Iowa.

4. W. C. Wildman, Alkaloids of the Amaryllidaceae, in R. H. Manske, ed. The Alkaloids, Vol. 6, p. 289, Academic Press, Inc., N.Y. (1961).

5. C. Djerassi, K. Mislow and M. Shamma, Experientia, 18, 53 (1962).

6. a) Full papers on the CD and ORD spectra of all of the compounds in this letter plus others are presently being prepared. b) G. G. DeAngelis, Tetrahedron 24, 5469 (1968).