

have made theoretical calculations of the $1/R^3$ force modifications of the spectrum to be expected for myristamide (using both of the angles given in Fig. 1). These calculations support the interpretation of the 2120–2250 Å. absorption as a crystal transition, in that the long-wave-length allowed component is predicted to occur in the a axis direction, split off by *ca.* 100 to 150 Å., just as observed (and regardless of which angle is chosen).

We have also made quantum-theoretical calculations of the direction of the transition moment for an amide model. In the model an amide is regarded as a perturbed allyl anion⁵ with the nitrogen represented by a deepening of the coulomb potential on one of the end carbon atoms and the oxygen considered as being the same as carbon. The result is that the direction should be close to the nitrogen–oxygen line, but inclined toward the carbon–nitrogen line. Of the two values found in our experiments the one with an angle of 9.1° from the nitrogen–oxygen line is thus favored. Both the experimental and theoretical aspects of this investigation will be reported in detail in a forthcoming paper.

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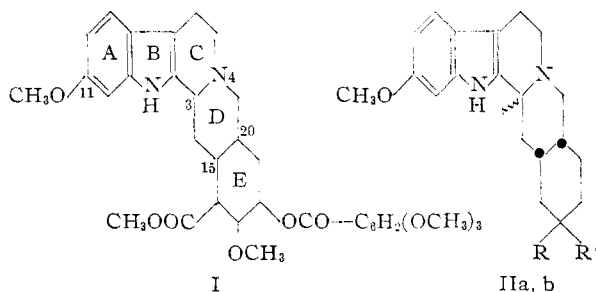
(5) Calculation was facilitated by use of full configuration interaction A.S.M.O. calculations on allyl anion (H. D. Hunt, D. L. Peterson and W. T. Simpson, to be published).

(6) National Science Foundation Predoctoral Fellow, 1954–1955.

THE D/E CIS RING JUNCTURE OF RESERPINE

Sir:

Reserpine, the potent hypotensive agent obtained from various species of *Rauwolfia*, has been assigned the structure I.^{1,2} Because of its proxi-



mate relation to deserpidine (formula I with the 11-methoxyl replaced by $-H$), Schlittler, *et al.*, surmised that reserpine too possesses a D/E *cis* (allo) ring juncture³; and Wintersteiner, *et al.*,⁴ on the basis of the intramolecular N-4 quaternization of methyl reserpate tosylate, inferred the same relationship. We wish to report for this view conclu-

(1) L. Dorfman, A. Furlenmeier, C. F. Huebner, R. Lucas, H. B. MacPhillamy, J. M. Müller, E. Schlittler, R. Schwyzer and A. F. St. André, *Helv. Chim. Acta*, **37**, 59 (1954).

(2) N. Neuss, H. E. Boaz and J. W. Forbes, *THIS JOURNAL*, **76**, 2463 (1954).

(3) H. B. MacPhillamy, L. Dorfman, C. F. Huebner, E. Schlittler and A. F. St. André, *ibid.*, **77**, 1071 (1955).

(4) P. A. Diassi, F. I. Weisenborn, C. M. Dylion and O. Wintersteiner, *ibid.*, **77**, 2028 (1955).

sive confirmation obtained through an 11-methoxyalloyohimbane (IIa, $R = R' = H$) (reserpine) synthesis which is stereochemically unambiguous insofar as the C_{15} – C_{20} asymmetric centers are concerned.⁵

6-Methoxytryptamine⁶ (obtained through the route: 6-methoxyindole \rightarrow 6-methoxygramine methosulfate \rightarrow 6-methoxyindoleacetonitrile \rightarrow 6-methoxytryptamine) was alkylated in boiling dimethylformamide by ethyl *dl-cis*-2-bromomethylcyclohexanecarboxylate,^{7,8} affording the lactam of *dl-cis*-N-(β -3'-indolylethyl)-2-aminomethylcyclohexanecarboxylic acid (III) (benzene solvate), m.p. 72.5 – 74.0° (Calcd. for $C_{20}H_{26}N_2O_2 \cdot C_6H_6$: C, 77.19; H, 7.97. Found: C, 77.02; H, 7.95). Heating III with phosphorus oxychloride in benzene, followed by platinum-catalyzed reduction of the unsaturated Δ^3 -ring-closed product, yielded the desired *dl*-allo base IIa, which melted at 209 – 210° after crystallization from methanol. Infrared spectral comparison of chloroform solutions of IIa and a reserpine derived by reduction of reserpone (IIb, $R, R' = O$)⁹ showed the two substances to be, apart from the racemic nature of the former, identical.¹⁰

Publication of our views on the nature of the remaining asymmetric centers in reserpine and deserpidine, including evidence relating thereto, is anticipated.

Acknowledgment.—The authors wish to express their gratitude to the Department of Health, Welfare and Education for financial support (Grant No. G-3892) and to S. B. Penick and Co. for a gift of reserpine.

(5) The matter of the stereochemistry at C_3 in our synthetic product is deferred for the present.

(6) S. Akabori and K. Saito, *Ber.*, **63B**, 2245 (1930).

(7) G. Stork and R. Hill, *THIS JOURNAL*, **76**, 949 (1954).

(8) Unpublished results obtained in this laboratory.

(9) C. F. Huebner, H. B. MacPhillamy, A. F. St. André and E. Schlittler, *THIS JOURNAL*, **77**, 472 (1955).

(10) We should like to thank Dr. Schlittler and Dr. St. André for their assistance in establishing the identity of the two specimens. In addition, our base IIa was shown to be identical with material obtained by them *via* a different synthetic route.

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POLY-GLUTAMYL PTERIDINE COENZYMES

Sir:

It was recently demonstrated that the conversion of serine to glycine by a bacterial extract is dependent upon DPN, Mn^{++} , pyridoxal phosphate, orthophosphate and catalytic levels of a new coenzyme, Co C.^{1,2} Co C is isolated from *Clostridium cylindrosporium*, and substitutes for but is not identical with known folic acid derivatives. By means of fractional acetone precipitation, chromatography on cellulose columns, and repeated paper chromatography in various solvent systems,³ five groups of pteridine derivatives with Co C activity have been separated in relatively pure form from extracts of

(1) B. E. Wright, *Biochim. et Biophys. Acta*, **16**, 165 (1955).

(2) B. E. Wright, *Fed. Proc.*, **14**, 308 (1955).

(3) B. E. Wright and E. R. Stadtman, unpublished data.