in the usual manner. Direct comparison of the X-ray powder diagrams[10] of the recrystallized picrate and of 2-methyladenine picrate proved their identity.

Ribose was identified in the filtrate from the resin column and 1-aminopropanol-2 in the ammoniacal eluate using paper chromatographic methods.[7,11]

The occurrence of 2-methyladenine in nature has not been observed previously. Many of the solvent systems employed in current paper chromatographic surveys of nucleic acid composition fail to differentiate 2-methyladenine from adenine.

(10) By Mr. R. B. Scott.

(11) S. M. Partridge, *Biochem. J.*, **42**, 238 (1945); *Nature*, **164**, 443 (1949); E. Chargaff, *et al.*, *J. Biol. Chem.*, **175**, 70 (1948).

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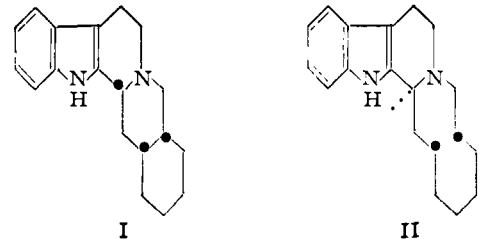
THE STEREOSPECIFIC SYNTHESIS OF *dl*-ALLOYOHIMBANE AND *dl*-3-EPIALLOYOHIMBANE

Sir:

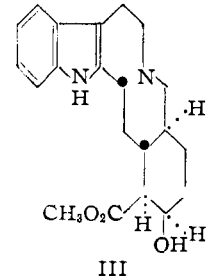
Three of the four possible steric arrangements of the ring system present in the yohimbe alkaloids have so far been found in nature: they are the ring systems present in yohimbane,[1] ψ-yohimbone[2] and alloyohimbane.[3]

In connection with the problem of the stereochemistry of the yohimbe alkaloids and closely related substances, such as reserpine,[4] it is important (a) to establish rigidly the stereochemistry of these systems[5]; (b) to synthesize the missing fourth isomer, 3-epialloyohimbane. Both of these goals have now been reached: *cis*-β-hydrindanone[6a] was prepared by cyclization of *cis*-cyclohexane-1,2-diacetic acid,[6b] itself made by ozonolysis of oxalyl β-decalone which was in turn prepared from crystalline *cis*-β-decalol, m.p. 105°,[6b] and *cis*-β-decalone. Subsequent steps were designed so as not to affect the *cis* junction established in the hydrindanone. Opening of the cyclic ketone by treatment with perbenzoic acid led to the lactone of *cis*-2-hydroxymethylcyclohexaneacetic acid, b.p. 115–120° (4 mm.). Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.37; H, 8.90. This could be opened with hydrogen bromide in alcohol to ethyl *cis*-2-bromomethylcyclohexaneacetate, b.p. 100–106° (1 mm.). Calcd. for $C_{11}H_{19}O_2Br$: C, 50.20; H, 7.28. Found: C, 50.45; H, 7.45. Heating the bromoester in dimethylformamide solution with tryptamine gave, after chromatography, *cis*-N-3-indolylethyl-octahydro-3-isoquinolone, m.p. 171–172°. Calcd. for $C_{19}H_{24}ON_2$: C, 76.99; H, 8.16. Found: C, 76.87; H, 8.02. Cyclization of the lactam with phosphorus oxychloride gave an unstable vinylamine which was immediately reduced catalytically to the saturated base (I), m.p. 143.5–144°. Calcd. for $C_{19}H_{24}N_2$: C, 81.38; H, 8.63. Found: C, 81.24; H, 8.51. Mixed melting point determination and comparison of infrared spectra demonstrated the identity of this base with *dl*-alloyohimbane.[7] Reduction of the vinylamine with sodium and alcohol in liquid ammonia solution gave the C_3 epimer (II) of *dl*-alloyohimbane, m.p. 185–186°. Found: C, 81.66; H, 8.65.

This synthesis, incidentally, demonstrates that alloyohimbane has a *cis*-decahydroisoquinoline system and the assumed stereochemistry shown in III[5] is therefore established for yohimbine.[8]



I II



III

(1) J. Jost, *Helv. Chim. Acta*, **32**, 1301 (1949).

(2) M. M. Janot, R. Goutarel and M. Amin, *Compt. rend.*, **230**, 2041 (1950); *cf.* footnote 5.

(3) A. Le Hir, R. Goutarel and M. M. Janot, *Compt. rend.*, **235**, 63 (1952).

(4) E. Schlittler, *et al.*, *Experientia*, **9**, 369 (1953).

(5) The correct stereochemistry of the yohimbe alkaloids was derived by one of us (see B. Witkop and S. Goodwin, THIS JOURNAL, **75**, 3371 (1953), footnote 6) and by M.-M. Janot, R. Goutarel, A. Le Hir, M. Amin, and V. Prelog, *Bull. soc. chim.*, 1085 (1952), on the basis of the existence in yohimbine of a *trans*-decahydroisoquinoline system. This assumption was however not rigidly established until the completion of the work described in this Communication, (*cf.* footnote 8), as it rested *either* on bigh temperature base degradations leading to octahydroisoquinolines with the double bond at, or adjacent to, the ring junction (B. Witkop, THIS JOURNAL, **71**, 2559 (1949)) *or* on an assumed, but unknown, course of the catalytic hydrogenation of sempervirine.[8]

(6) (a) A. Kandiah, *J. Chem. Soc.*, **922** (1931). (b) W. Hückel and H. Friedrich, *Ann.*, **451**, 132 (1926).

(7) We wish to thank Dr. Janot for his kindness in making this sample available.

(8) This stereochemistry is further confirmed by the synthesis of *dl*-yohimbane by Van Tamelen and Shamma who independently carried out a similar series of transformations starting with *trans*-β-hydrindanone (see accompanying communication).

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A NEW METHOD FOR IDENTIFYING C-TERMINAL RESIDUES IN PEPTIDES

Sir:

Although there are several satisfactory methods for the identification of N-terminal residues in peptides,[1,2] there are few methods for the identification of C-terminal residues. We have recently investigated the thiohydantoin method discovered

(1) H. G. Khorana, *Quart. Rev.*, **6**, 340 (1952).

(2) P. Desnuelle, "Advances in Enzymology," Vol. 14, Interscience Publishers, Inc., New York, N. Y., 1953.