

We therefore propose that deserpidine and reserpine are derivatives of 3-epi- $\alpha$ -yohimbine.

Regarding the stereochemistry of the substituents in ring E of these alkaloids, we feel that the formation of the  $\gamma$ -lactone of reserpic acid<sup>3</sup> and of deserpidic acid together with other evidence which we have obtained from elimination reactions, point to an all *cis* configuration.

Although we do not believe that the relationship between C-15 and C-16 has been sufficiently established in the case of  $\alpha$ -yohimbine<sup>4,7</sup> to permit at this time the definite assignment of a complete configuration to deserpidine and reserpine, we do favor the one expressed in formula I.

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### RESOLUTION AND SYNTHESIS OF AN OPTICALLY ACTIVE FLUORO COMPLEX

Sir:

The role of fluoride ion in complex formation has been of especial interest in studies on bond type in coordination compounds.<sup>1,2</sup> Magnetic evidence has indicated that fluoride is capable of forming bonds with trivalent cobalt of the extreme ionic type, *viz.*, in  $[\text{CoF}_6]^{3-}$ , but is also able to enter into covalent bond formation when present in partially substituted cobalt amines.<sup>3</sup> Except for the information inferred from the fact that the latter type of complexes are diamagnetic, little is known about the nature of the Co-F bond in these complexes.

We have recently succeeded in resolving the complex, *cis*- $[\text{Co en}_2\text{F}_2]^+$  (I) by use of *l*-dibenzoyltartaric acid (II) and have prepared (I), as well as *cis*- $[\text{Co en}_2\text{NH}_3\text{F}]^{+2}$  (III), in active form through reactions of the analogous chloro complexes. This is believed to be the first instance in which a complex containing coordinated fluoride has been resolved.

The resolution consisted in bringing together stoichiometric quantities of *cis*- $[\text{Co en}_2\text{F}_2]^+$ ,  $\text{Ag}_2\text{CO}_3$  and (II), removing  $\text{AgI}$  and precipitating the *d*- $[\text{Co en}_2\text{F}_2]^+$  salt of (II) with acetone. Purification of the latter was effected by dissolving it in a small quantity of water and chilling sharply, whereby a crystalline product was obtained having  $[\alpha]^{25\text{D}} +120^\circ$ . The resolving agent was removed by triturating the diastereomer with acetone containing a little concd.  $\text{HNO}_3$ , yielding thereby *d*- $[\text{Co en}_2\text{F}_2]\text{NO}_3$  with  $[\alpha]^{25\text{D}} +220$ .

Active (I) was also prepared by the reaction of *l*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$  ( $[\alpha]_{\text{D}} +610$ ) in 1:1 ethanol-HF, in which an excess of  $\text{Ag}_2\text{CO}_3$  had been dissolved. For the purified substance, isolated as the nitrate,  $[\alpha]^{25\text{D}} +220$ . The *dextro* isomer of (III) was prepared in like manner by starting with *d*- $[\text{Co en}_2\text{NH}_3\text{Cl}]\text{Cl}_2$  ( $[\alpha]_{\text{D}} +140^\circ$ ). For the bromide of

(1) W. C. Fernelius, *Record Chem. Progress (Kresge-Hooker Sci. Lib.)*, **2**, 17 (1950).

(2) H. Taube, *Chem. Rev.*, **50**, 69 (1952).

(3) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, pp. 116-117.

(III),  $[\alpha]^{25\text{D}} +170$ . The salts of (I) and (III) were isolated in microcrystalline form, that of (I) being red, and that of (III) being salmon in color.

Kinetic studies now in progress on a number of cobalt fluoro complexes indicate that the rates of racemization and aquation are slower than those of the analogous chloro complex. At  $35^\circ$  in 0.1 *N*  $\text{HNO}_3$  (I) mutarotates to about one half the original rotation at a moderate rate (half-life, 1 hr.) and then loses its remaining activity over a period of several days. A study of the reactions undergone by the active fluoro complexes with a number of reagents to determine the nature of active products is also being undertaken.

A more detailed account of this work as well as other results will be communicated in the near future.

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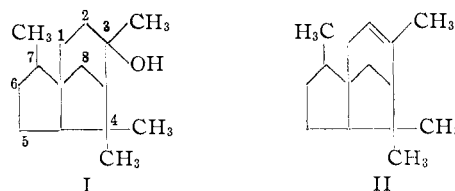
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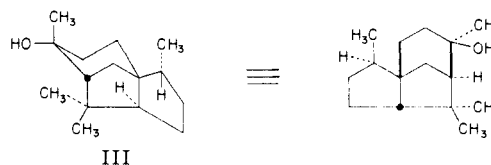
### THE TOTAL SYNTHESIS OF CEDROL AND CEDRENE

Sir:

We have recently outlined the considerations which led us to propose structure I for the tricyclic sesquiterpene cedrol<sup>1</sup> and II for the related cedrene.



Our communications on the subject did not deal with the stereochemistry of the five asymmetric centers present in I, but various considerations have led us to consider III the most likely representation of the stereochemistry of cedrol.



We have now completed an unambiguous, stereospecific total synthesis of cedrol which confirms the stereochemistry illustrated by formula III and incidentally provides unambiguous proof that no rearrangement is involved in the dehydration of cedrol to cedrene:

Diethyl 4,4-dimethyl-5-keto-1,3-cyclopentane dicarboxylate<sup>2</sup> was alkylated with benzyl  $\alpha$ -bromopropionate, and the resulting triester was hydrogenated over palladium charcoal to the acid IV, m.p. 113-115 $^\circ$ . (Found: C, 58.47; H, 7.43).

(1) G. Stork and R. Breslow, *THIS JOURNAL*, **75**, 3291 (1953).

(2) Cf. C. S. Gibson, K. V. Hariharan and J. L. Simonsen, *J. Chem. Soc.*, **3009** (1927).