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THE STRUCTURE OF PIPTANTHINE
A CATALYTIC EPIMERIZATION OF ORMOSIA ALKALOIDS

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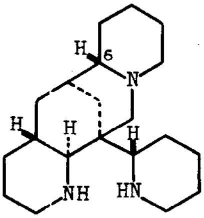
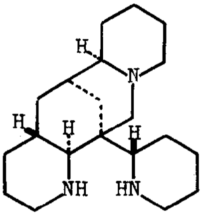
The elementary composition, functional groups and some reactions of piptanthine, $C_{20}H_{35}N_3$, m.p. 142-143°, an alkaloid of <u>Piptanthus nanus</u>, have been described by Eisner and Šorm (1). These authors found that one of the nitrogen atoms is tertiary, while the remaining two are secondary and can be bridged on treatment with phosgene to give a urea, homoxypiptanthine, $C_{21}H_{33}N_3O$, m.p. 153-155°. No double-bonds, C-methyl groups or N-alkyl group were found in the molecule. A possible relationship of piptanthine to <u>Ormosia</u> alkaloids was suggested (1).

Recently, Karle and Karle (2) determined the structure and stereochemistry of jamine, $C_{21}H_{35}N_3$ (3), the formaldehyde adduct of ormosanine, $C_{20}H_{35}N_3$, by X-ray crystallography. Their analysis leads to formulation I for ormosanine. We have now been able to perform a surprisingly simple transformation of ormosanine to piptanthine, on the basis of which piptanthine must be an epimer of ormosanine at C_6 and possess structure II.



I



II

Prolonged treatment of ormosanine with platinum in acetic acid in a hydrogen atmosphere at room temperature led to the formation of a new compound; the progress of this reaction was followed by thin-layer chromatography. This compound was found to be identical by infrared and N.M.R. spectroscopy and by T.L.C. with an authentic sample of piptanthine.[*] Furthermore, the corresponding homoxy derivatives were indistinguishable. The following findings reveal the nature of this transformation. Homoxy-ormosanine (III), $C_{21}H_{33}N_3O$, the urea derivative of ormosanine, was converted to homoxypiptanthine under similar conditions. This clearly shows that the tertiary nitrogen is involved in the reaction, since a dehydrogenation-hydrogenation process involving a hydrogen atom α to a nonbasic urea nitrogen is highly unlikely. Furthermore, homoxy-ormosanine shows Bohlmann bands in the 2800 cm^{-1} region of its infrared

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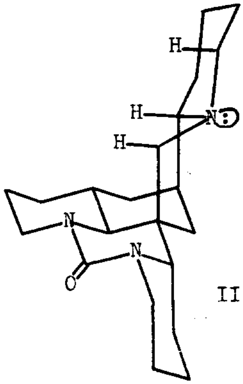
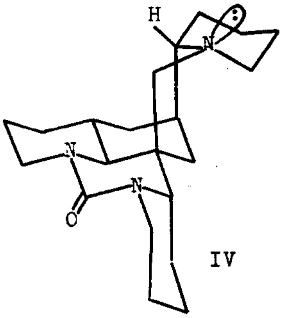
[*] We thank the Czech workers (1) for a sample of the alkaloid. Since natural ormosanine is racemic (3), the catalytically produced piptanthine is also racemic. Piptanthine from *P. nanus* is levorotatory ($[\alpha]_D$ -24.3°) (4). The absolute configuration of the optically active *Ormosia* alkaloids is unknown and none is implied in this communication.

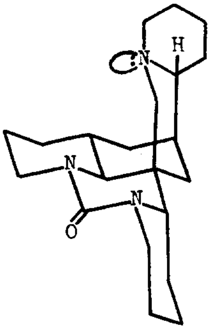
spectrum of *a KBr pellet* indicative of the *trans* diaxial arrangement of the tertiary nitrogen electron pair and at least two α hydrogens (5) and in agreement with conformation III (2), while its corresponding *solution* spectrum ($CHCl_3$) shows no Bohlmann bands and indicates conformation IV or V for homoxy-ormosanine in solution. In contrast, piptanthine and homoxypiptanthine show Bohlmann bands under all conditions in agreement with the stable conformation VI. This analysis is in excellent agreement with a configurational change at C_6 in the essentially irreversible catalytic transformation I→II.



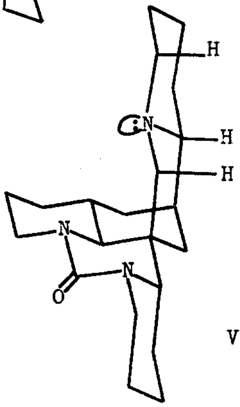
III



IV

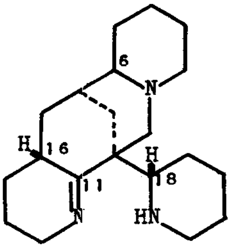


V

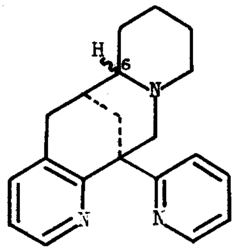


VI

The discovery of this specific epimerization necessitates a revision of two recently reported configurational assignments. Panamine, $C_{20}H_{33}N_3$, an alkaloid of *Ormosia panamensis*, has been reported to give ormosanine (I) on reduction with sodium borohydride and two products, ormosanine and its isomer, $C_{20}H_{35}N_3$, m.p. 136–137°, $[\alpha]_{589}$ +23°, on catalytic hydrogenation (3). It was proposed (3) that the probable structure of panamine is VII and that the new isomer, m.p. 136–137°, must be an epimer of ormosanine (I) at C_{11} with a C_{11},C_{16}-*cis*-juncture. We now find that this isomer is, in fact, identical with piptanthine (II).[*]



VII



VIII

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[*] Since piptanthine arising from panamine is dextrarotatory, while that from *P. nanus* is levorotatory, our correlation shows that the two naturally occurring alkaloids, panamine and piptanthine, belong to antipodal series.

It has undoubtedly arisen by a catalytic isomerization of the primary reduction product, ormosanine. Although formula VII for panamine is not disproved by this new finding, one argument for the placement of the unsaturation at C_{11} is clearly lost.

It has also been reported that the catalytic dehydrogenation of ormosanine and panamine leads to the pyridine VIII[*] in which a β hydrogen atom at C_6 was assumed in analogy to ormosanine (7). Our recent evidence (Bohlmann bands, reduction experiments) makes it quite clear that VIII must have the piptanthine stereochemistry at C_6 (α hydrogen atom); the reported epimerization therefore also takes place during the catalytic dehydrogenation.

Acknowledgments--The support in the form of a Shell Canada Fellowship (P.D.) and a National Research Council, Ottawa, Scholarship (J.S.W.) is gratefully acknowledged.

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[*] The reported product of a mild dehydrogenation of the alkaloid ormojanine (6) has now been found to be identical with pyridine VIII.

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