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# DEHYDROGENATION OF THREE ORMOSIA ALKALOIDS

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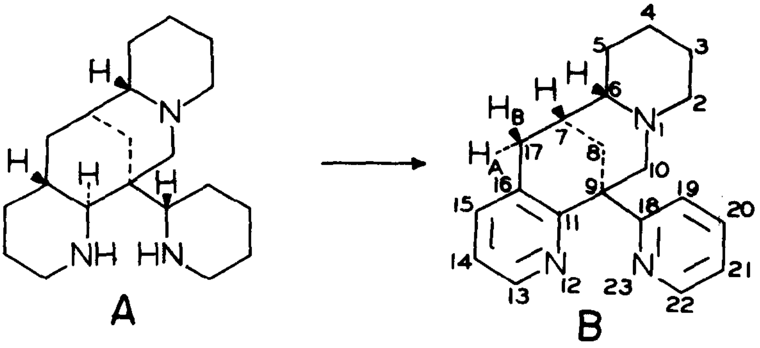
Dehydrogenation of the <u>Ormosia</u> alkaloids ormosinine (OP I), ormosanine (OP II) and panamine (OP III) leads to a common product consistent with the structure of the alkaloids shown in the accompanying papers (1), confirming the interrelationship there described.

On heating with 5% palladized charcoal at 250° for 25 min., (racemic) OP II (A) evolves gases which, when led through an ethereal picric acid solution, deposit ammonium picrate. Chromatography of the residue over silicic acid produces a 23% yield of dehydroormosanine (DOP II) (B), which, on crystallization from ethanol, has m.p. 146-147° and 154°; $\lambda_{max}$ 263 mμ



(log ε 3.88). The NMR spectrum (2) showed complex groups at $\delta$ = 8.58 and $\delta$ = 8.21 p.p.m. (two protons, α-protons of pyridine rings), and at $\delta$ = 7.76-6.85 p.p.m. (five protons, β- and γ-protons of pyridine rings). This pattern reveals two pyridine rings, one substituted only at an α-position, and the other substituted at α- and β-positions. In the region of benzylic protons there appears the AB portion of an ABX pattern: a doublet centered at $\delta$ = 2.81 p.p.m. ($H_{17A}$ coupled to $H_{17B}$, J = 11 c.p.s.) and a quartet at $\delta$ = 3.31 p.p.m. ($H_{17B}$, coupled to $H_{17A}$ and to $H_7$, J = 2.5 c.p.s.). At $\delta$ = 3.03 p.p.m. appears a poorly resolved peak for two protons arising from the methylene group at $C_{10}$. The mass spectrum confirms the elemental formula and shows peaks at m/e 207 and 222; a peak at m/e 98, which also appears in the spectrum of the parent alkaloids, evidently arises from the quinolizidine moiety.

When OP I was treated in this manner, the product was the dextrorotatory form of DOP II, m.p. 132-133°, $[\alpha]_{589}$ + 120°, $[\alpha]_{436}$ + 246° (c 1.21, ethanol), identical in ultraviolet and infrared spectra and in chromatographic behavior with DOP II. Treatment of the more unstable OP III by such procedures proved very difficult, but the dihydro OP III (levorotatory OP II) was converted to dextrorotatory DOP II identical in all respects with the material from OP I.

Hydrogenation of DOP II in 1 N HCl at atmospheric pressure stopped after the uptake of three moles of hydrogen. The product, which produced a single peak on gas chromatography, showed spectral properties consistent with hexahydro DOP II. The infrared spectrum showed peaks at 750 and 785 cm.$^{-1}$, characteristic of three adjacent protons on a pyridine ring. The ultraviolet spectrum ($\lambda_{max}$ 272 mμ, log ε = 3.51) and the NMR peaks in the aromatic region corresponded to 2,3-lutidine. The catalytic reduction therefore affected only the unhindered monosubstituted pyridine ring.

Hydrogenation of hexahydro-DOP II in 1 N HCl under 45 p.s.i. gave an oily mixture from which dodecahydro-DOP II, $C_{20}H_{35}N_3$, could be crystallized in ethyl acetate, m.p. 181-182°. This material had the same retention time in gas chromatography as OP II, but differed in infrared spectrum, and gave a mixture melting point depression. Dodecahydro-DOP II readily added formaldehyde in ethanol solution to produce an N,N-methylene adduct with a retention time different from that of OP VI on gas chromatography. Dodecahydro-DOP II must therefore be epimeric with OP II at one or more of $C_{11}$, $C_{16}$ and $C_{18}$. Synthetic studies directed towards DOP II are in progress.

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## REFERENCES

[1] P. Naegeli, W. C. Wildman and H. A. Lloyd, Tetrahedron Letters, 2069, (1963); I. L. Karle and J. Karle, Tetrahedron Letters, 2065, (1963).

[2] NMR spectra were determined on a Varian A-60 spectrometer in deuterochloroform with tetramethylsilane ($\delta = 0$) as an internal standard.