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STRUCTURE RELATIONSHIPS IN THE ORMOSIA ALKALOIDS

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The seeds of Ormosia panamensis and O. jamaicensis yielded a new alkaloid, jamine (OP VI), $C_{21}H_{35}N_3$, m.p. 153-154°, [α] 0.0°. This alkaloid proved to be identical in all respects (1) to the reaction product of formaldehyde with another alkaloid isolated from the same Ormosia species, ormosanine (2) (OP II), $C_{20}H_{35}N_3$, m.p. 183-184°, [α] 0.0°. OP II is most probably identical to piptamine (3) (m.p. 173-174°; formaldehyde adduct (m.p. 147-148°), an alkaloid isolated from Piptanthus nanus and to "alkaloid A" (4) isolated from O. jamaicensis. Both OP II and OP VI are racemic. A partial resolution of OP VI was accomplished with dibenzoyltartaric acid yielding a glass $[\alpha]_{589}$ +7.9°, $[\alpha]_{436}$ + 13° and an oil $[\alpha]_{589}$ -3.8°, $[\alpha]_{420}$ -7.0°.

X-ray analysis (5) established the structure of OP VI as A; therefore OP II must have structure B. The knowledge of the structure for OP II permitted us to derive the structures of two other Ormosia alkaloids by chemical methods. Ormosinine (2) (OP I) and panamine (2) (OP III), two Ormosia

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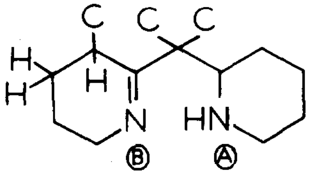
alkaloids of formula $C_{20}H_{33}N_3$, were converted into derivatives of OP II and their probably structures are established below as C and D respectively.

Sodium borohydride reduction of OP III (oil, $[\alpha]_{589}$ -11.0°, $[\alpha]_{436}$ - -21.3°, diperchlorate, m.p. 285-287°) gave a single product, levorotatory OP II, an oil, $[\alpha]_{589}$ -19°, $[\alpha]_{436}$ -39°. This material had the same IR (CCl_4) and NMR spectra as OP II and the same retention time in gas chromatography. Its formaldehyde adduct (m.p. 116-117°, $[\alpha]_{589}$ -1.6°, $[\alpha]_{436}$ -3°) and OP VI, had identical IR (CCl_4) and NMR spectra.

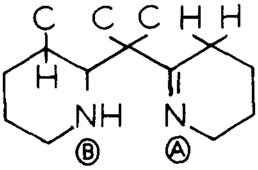
Catalytic reduction of OP III with PtO_2 in dilute HCl (6) followed by chromatography over silica gel produced two isomers in approximate 1/2 ratio. The major product was identified as levorotatory OP II. The other compound was a crystalline isomer (m.p. 136-137°), $[\alpha]_{589}$ +23°, $[\alpha]_{436}$ +38°). Its IR (CCl_4) and NMR spectra, its retention time on gas chromatography and its formaldehyde adduct (m.p. 181-186°, $[\alpha]_{589}$ +34.5°, $[\alpha]_{436}$ +65°) were different from those of OP II. Since the double bond in OP III is located as shown in (D) (see below) this other isomer must have a <u>cis</u> junction (E).

The other alkaloid OP I (m.p. 220-222°, $[\alpha]_{589}$ +9.6°, $[\alpha]_{436}$ +14.9°) could be catalytically reduced only with great difficulty to traces of material having the same retention time on vapor phase chromatography as OP II, and giving the same type of formaldehyde adduct to confirm the relationship. OP I was converted into a derivative of OP III in the following manner: Treatment of OP I with formic acid gave an oily N-formyl derivative which upon $LiAlH_4$ reduction yielded a compound identical (1) in all respects to N-methyl OP III, $C_{21}H_{35}N_3$ (m.p and mixed m.p. 103°; $[\alpha]_{589}$ +5°; $[\alpha]_{436}$ +19°; monomethiodide m.p. 209-211°; dihydro derivative m.p. 119-120°, $[\alpha]_{589}$ -43°, $[\alpha]_{436}$ -87°). N-methyl OP III was prepared also by $LiAlH_4$ reduction of the formamide of OP III itself or by reductive methylation, under neutral conditions, of the alkaloid with formaldehyde in the presence of Pd/C. The two formamides (oils) appear to be identical (NMR, IR, rotation) and therefore formic acid must rearrange one center in OP I to the configuration it possesses in OP III.

Study of the NMR and mass spectra led to the placement of the double bond in OP I and OP III. The spectra of the two alkaloids contain no olefinic proton signal, nor any signal that could arise from the grouping -HC=N- (7). A broad signal for one proton is observed at δ= 3.48 ppm for OP I and at δ= 3.57 ppm for OP III. These cannot be NH protons since the same peak is present in N-methyl OP III (one proton δ= 3.38 ppm) but not in dihydro N-methyl OP III. These facts are consistent with formula F but not with G. Another argument in favor of placing the double bond on nitrogen B in both OP I and OP III is that the mass spectra of the two alkaloids are identical and the piperidyl cation (m/e 84) is prominent in both cases while the monounsaturated piperidyl cation (m/e 82) is insignificant.



F

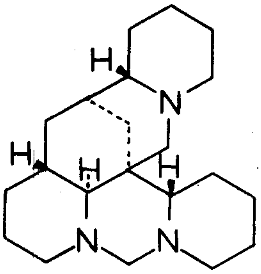


G

A series of Hofmann degradations was carried out on derivatives of OP III and the resulting unusual reactions which are in accord with the above structures will be reported in the full paper.

Finally, OP I and OP III were dehydrogenated to a common product identified as dextrorotatory dehydro OP II (8).

We wish to thank Dr. H. M. Fales for many helpful discussions.



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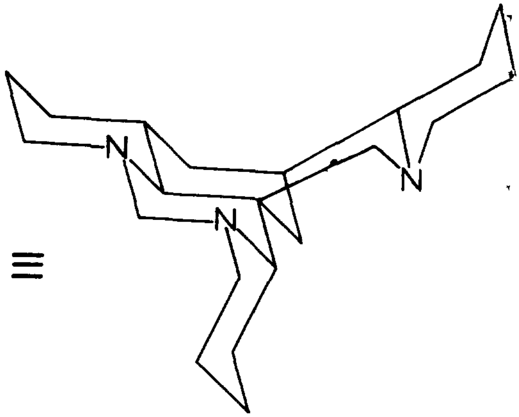
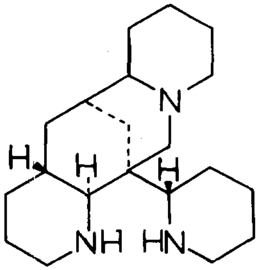
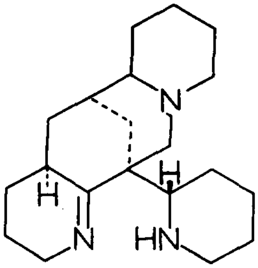




B



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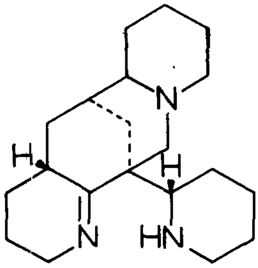
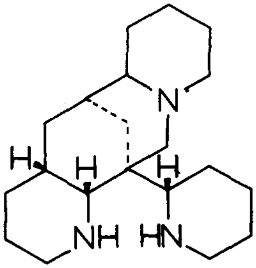


D



E

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[1] Same IR$_{\text{nujol}}$, IR$_{CCl_4}$, m.p. and mixed m.p., $[\alpha]_{589}$, $[\alpha]_{436}$, NMR, mass spectrum, retention time on gas chromatography.

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[6] Under neutral conditions no reduction was observed.

[7] Such a proton in $(CH_3)_3\text{-C-N=}\underline{CH}\text{-}CH_3$ gives rise to a quarter centered at δ= 7.77 p.p.m.

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All the compounds reported gave satisfactory analyses. The m.p. were taken on the Kofler block, the NMR were determined on a Varian A-60 spectrometer and all the rotations were measured in ethanol.