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THE MOLECULAR STRUCTURE OF ORMOJINE, AN ALKALOID OF ORMOSIA JAMAICENSIS

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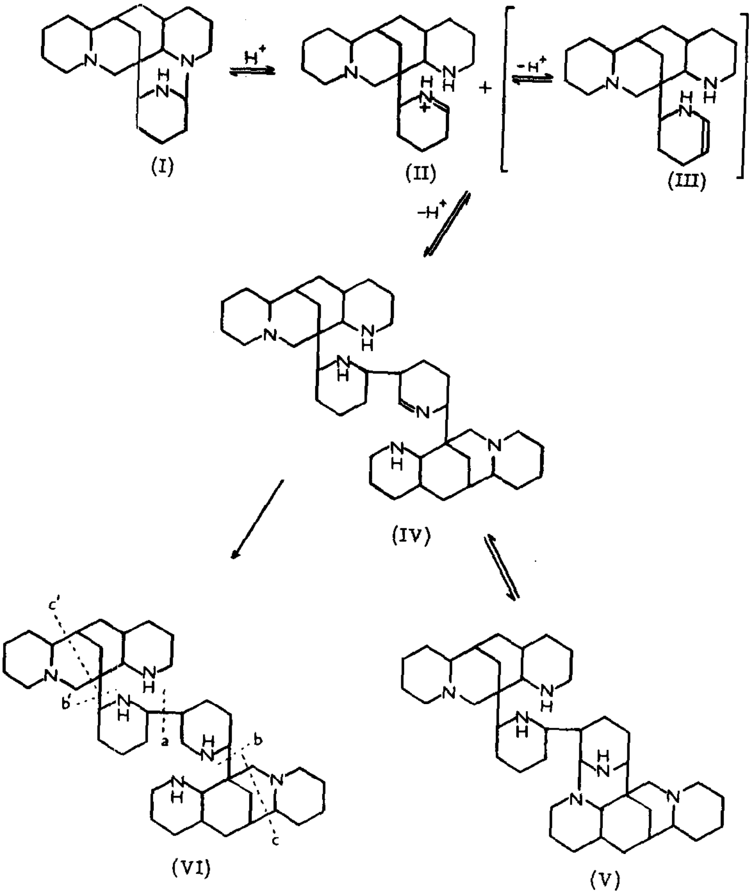
Investigations by Karle and Karle, using X-ray diffraction have recently established the structures and the stereochemistry of panamine(1) and jamine, (2, 3) alkaloids derived from extracts of Ormosia panamensis(4) and O.jamaicensis, (4) respectively. Five related alkaloids were isolated from the seeds of O.jamaicensis in an earlier study.(5, 6) Comparison of the chemical properties, and the infrared and mass spectra of one of these alkaloids, ormosajine, $C_{20}H_{33}N_3$, $[\alpha]_D + 23^{\circ}$, with those of the isomer, panamine,(7) has indicated that these compounds differ in configuration but have the same structure (I).(8)

Treatment of either ormosajine or ormojine, another alkaloid of O.jamaicensis, (5, 6) with dilute hydrochloric acid gave an equilibrium mixture containing both alkaloids as major constituents. With the knowledge of the structure of ormosajine, it became possible to interpret the reactions involved in the interconversion of ormojine and ormosajine.

Contrary to an earlier observation, (5) it was found that the mass spectrum of ormojine provided evidence of a


(I)
H⁺
(II)
+
-H⁺
(III)
-H⁺
(IV)
(VI)
a
b
b'
c
c'
(V)

parent ion, m/e 630; a high resolution measurement indicated that this ion had the formula $C_{40}H_{66}N_6^+$ and established that ormojine was formed through dimerisation of ormosajine. The p.m.r. spectrum of ormojine included a signal at τ, 6.58 due to one proton in the system N-CHR-N, but the absence of signals at lower τ values and of absorptions in the olefinic and azomethine (1650 cm.$^{-1}$) (9) regions of the infrared spectrum established that these unsaturated functions were absent. Treatment of ormojine with sodium borohydride in ethanol gave a dihydroderivative, m.p. 153-155°, that was stable in dilute acid. The p.m.r. spectrum of this derivative did not include a signal in the region τ, 6.58. Evidently, in accord with precedents, (8,10) reduction of the N-CHR-N system had occurred. The mass spectrum of dihydro-ormojine (VI) confirmed the formula, $C_{40}H_{68}N_6$ (accurate mass study of parent ion, m/e 632) and showed that the major product of electron bombardment was the ion, m/e 316 ($C_{20}H_{34}N_3^+$) which could result from cleavage of the molecule (VI) at "a". The ions m/e 399 ($C_{25}H_{43}N_4^+$) and m/e 534 probably arose from fission at "b" (or b') and "c" (or c') respectively.(11)

We attribute the dimerisation of ormosajine (I) to initial protonation of the N-CHR-N system, followed by interaction of the azomethine (II) and the enamine (III) which are formed; the process is analogous to the dimerisation of Δ^1-piperideine(12) and of $\Delta^{1,6}$ (and Δ^{16})-dehydrosparteine.(13) The formation of ormojine (V) from the azomethine (IV) is similar to the process proposed for the conversion of the intermediate (II) to ormosajine (I).

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