

We consider the partial structure (XV) as a biogenetically plausible, but unproved working hypothesis for the A, B and nitrogen rings of delphinine. This partial formula coincides to some extent with a structure proposal of Jacobs¹ which in turn is based on the typical diterpenoid alkaloid system.⁶

We intend to discuss the merits of (XV) and the complete structure of delphinine in conjunction with some experimental studies now in progress.

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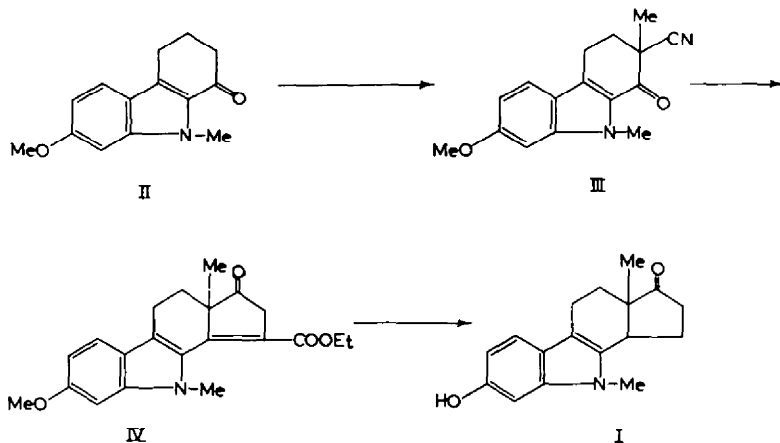
* Holder of an Eli Lilly postdoctoral fellowship.

• K. Wiesner, D. R. Armstrong, M. F. Bartlett and J. A. Edwards, *Chem. & Ind.* 132 (1954); *J. Amer. Chem. Soc.* 76, 6068 (1954).

Synthesis of 3-Desoxy-B-nor-6-aza-D-homoequilenin

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THE synthesis of the pyrrolo analogue (I) of equilenin was attempted on the lines of the synthesis of thiopheno¹ and furano² steroids reported earlier by us. 7-Methoxy-9-methyl-1-oxo-1:2:3:4-tetrahydrocarbazole (II), m.p. 130°, prepared in three steps from 2-hydroxymethylencyclohexanone and *m*-methoxybenzenediazonium chloride, was converted into 2-cyano-2:9-dimethyl-7-methoxy-1-oxo-1:2:3:4-tetrahydrocarbazole (III), m.p. 156°, in the usual manner.^{1,3} Compound (III), however, could not be converted into the tetracyclic pyrrolo-derivative (IV) by Stobbe condensation with diethyl succinate.

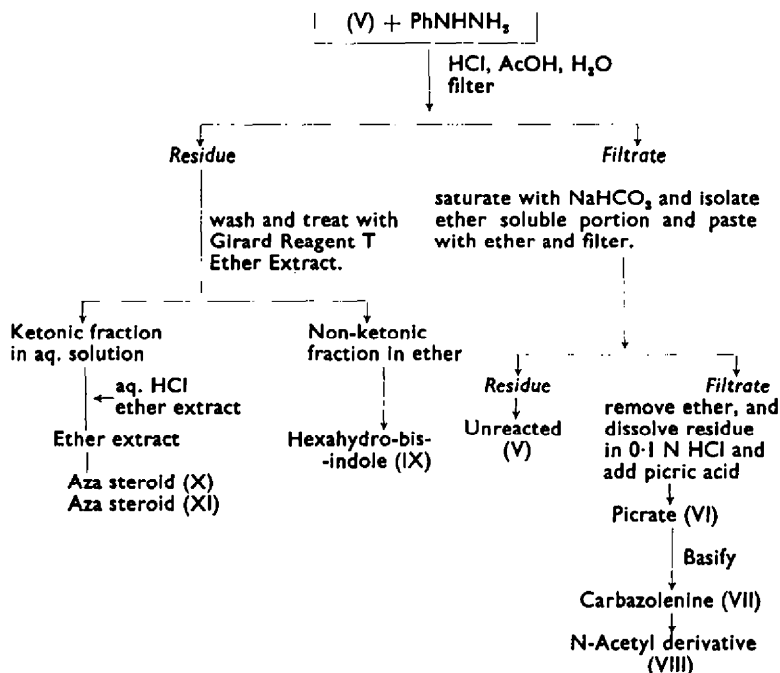


The synthesis of pyrrolo-steroids by an alternative route starting from *trans*-decalin-1:5-dione (V) was then undertaken. The latter (1 mol) and phenylhydrazine (1 mol) were boiled together in acetic

¹ R. B. Mitra and B. D. Tilak, *J. Sci. Industr. Res. India* 15 B, 573 (1956) *Chem. Abstr.* 51, 8790 (1957) and earlier papers.

² G. V. Bhide, N. L. Tikotkar and B. D. Tilak, *Chem. & Ind.* 1319 (1957).

acid for 14 hr followed by addition of hydrochloric acid. The mixture was boiled for a further 5 min, diluted with water, left overnight at 0° and then worked up as shown in the chart:—



The following compounds were isolated as shown in the chart above (analytical values of the compounds are given in Table 1):—*cis*-4:11,2':3'-(1'-oxocyclohexano)-1:2:3:4-tetrahydrocarbazolenine (VII), white prisms (petroleum ether, b.p. 40–60°), m.p. 168° (shrinks at 158°). Picrate (VI), yellow needles (acetone), m.p. 197°. Compound (VII) gave the N-acetyl derivative (VIII) [white prisms (petroleum ether b.p. 60–80°), m.p. 136°] and a semicarbazone (VIIIa), white plates (ethanol), m.p. 251°.

The carbazolenine (VII) has been assigned the *cis*-configuration in analogy with the observations of Georgian³ and on the basis of its facile conversion to compound (VIII) and a study of its Courtauld atomic model.⁴

TABLE I

Compound No.	Mol. formula	Required %			Found %		
		C	H	N	C	H	N
II	C ₁₄ H ₁₅ NO ₂	73.4	6.5	5.8	73.3	6.8	5.9
III	C ₁₆ H ₁₆ N ₂ O ₂	71.2	5.5	9.7	71.6	6.0	10.4
VI	C ₂₂ H ₂₀ N ₄ O ₈	56.4	4.3	12.0	56.7	4.5	12.4
VII	C ₁₆ H ₁₇ NO	80.3	7.2	5.85	80.7	7.2	5.6
VIII	C ₁₈ H ₁₉ NO ₂	76.8	6.8	5.0	76.6	6.6	4.7
VIIIa	C ₁₇ H ₂₀ N ₄ O	68.9	6.8	18.9	68.8	6.8	18.8
IX	C ₂₂ H ₂₀ N ₂	84.6	6.4	9.0	83.9	6.3	9.3
X	C ₁₆ H ₁₇ NO	80.3	7.2	5.85	80.7	7.6	5.6
XI	C ₁₆ H ₁₅ NO	81.0	6.4	5.9	80.9	5.6	6.0

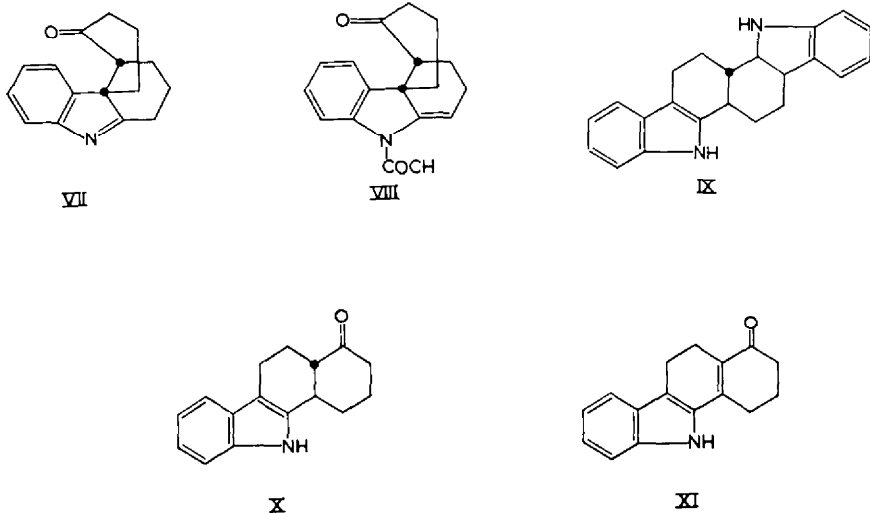
³ V. Georgian, *Chem. & Ind.* 1124 (1957).

⁴ R. Robinson, *Disc. Faraday Soc.* 16, 125 (1954).

The non-ketonic acid-insoluble fraction yielded 3:4:7:8:9:10-hexahydronaphtho-bis-(1:2-b, 5:6-b') indole (IX) [pale brown needles (ethanol), m.p. 305–307°] which was isolated through its picrate [dark brown prisms (benzene), m.p. 235–40° (dec.)]. The cyclisation of *cis*- and *trans*-decalin-1:5-dione-diphenylhydrazone has been studied by Hudson and Robinson.⁵ Whereas the *cis*-derivative gave a *cis*-bisindole, m.p. 312–316° (dec.), the *trans*-derivative gave an oxygen-containing nitrogenous compound m.p. 292–96° (dec.) which did not analyse correctly and showed the presence of oxygen.⁵

The acid-insoluble ketonic fraction gave compounds (X) and (XI) which were separated by fractional crystallisation. Compound (XI) was also obtained in the pure form by chromatography on alumina. *Trans*-3-desoxy-B-nor-6-aza-D-homoequilenin (X), m.p. 195°, crystallised in white flakes from methanol. 13:14-Dehydro-3-desoxy-B-nor-6-aza-D-homoequilenin (XI), m.p. 232–35° (softens at 225°), crystallised in yellow prisms from methanol.

The *trans*-configuration has been assigned to compound (X) in view of its synthesis from compound (V). The structures assigned to compounds (VII), (IX), (X) and (XI) were confirmed by their u.v. spectra and the infra-red spectrum of compound (XI). The spectra were compared with the u.v. and infra-red spectra of 1:2:3:4-tetrahydrocarbazole.



The infra-red spectra of 1:2:3:4-tetrahydrocarbazole and compounds (VII) and (XI) were determined in Nujol mull and the ultra-violet spectra were determined in ethanol solution. The principal absorption maxima and minima are as follows:—

1:2:3:4-Tetrahydrocarbazole

λ_{\max} : 228, 283, 338 $m\mu$ ($\log \epsilon = 4.520, 3.820, 0.290$)

λ_{\min} : 250, 336 $m\mu$ ($\log \epsilon = 3.290, 0.282$)

Infra-red absorption bands:—3420, 2940, 1460, 1365, 1330, 1308 cm^{-1} .

Carbazolenine (VII)

(cf. Witkop and Patrick,⁶ and Georgian⁵)

λ_{\max} 259 $m\mu$ ($\log \epsilon = 3.703$)

λ_{\min} 238 $m\mu$ ($\log \epsilon = 3.505$)

Infra-red absorption bands:—2890, 1720, 1590, 1460–1407, 1380, 1240, 1184–1191, 1125, 1030, 907, 775, 758, 752 cm^{-1} .

Hexahydro-bis-indole (IX)

λ_{\max} 232, 284, 334 $m\mu$ ($\log \epsilon = 4.863, 4.259, 2.465$)

λ_{\min} 252, 328 $m\mu$ ($\log \epsilon = 3.851, 2.335$)

⁵ B. J. F. Hudson and R. Robinson, *J. Chem. Soc.* 691 (1942).

⁶ B. Witkop and J. B. Patrick, *J. Amer. Chem. Soc.* 73, 1558 (1951).

Aza-steroid (X) λ_{\max} 225, 284 m μ (log ϵ = 4.528, 3.938) λ_{\min} 250 m μ (log ϵ = 3.534)*Aza-steroid (XI)* λ_{\max} 255, 393 m μ (log ϵ = 4.041, 4.2492) λ_{\min} 235, 290 m μ (log ϵ = 3.996, 3.218)Infra-red absorption bands:—3300, 2930, 1630, 1530, 1455, 1360, 1295, 1190 cm⁻¹.

Starting from compound(V) and *m*-methoxyphenylhydrazine, a synthesis of the desired 3-oxy-derivative of compound (X) appears possible although problems in isomer separation will then arise. Although the above synthesis leads to several reaction products, it is nevertheless of interest in view of the fact that a complex steroidal skeleton is built up in one step starting from readily accessible intermediates.

It is hoped that a detailed account of the work will be published in *Tetrahedron* in the near future.

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The hydration heat of the benzenesulphonate ion

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ONE mole of a solid salt MX may be directly dissolved in excess of water to form hydrated ions, when the enthalpy change is equal to the total heat of solution S ; alternatively it may first be split up into gaseous ions, with enthalpy change U equal to the lattice energy, and the ions then hydrated, with enthalpy change H . It follows that

$$S = U + H, \quad (1)$$

and the hydration heat of the pair of gaseous ions M^+ and X^- may be derived if values of U and S are known. Although only hydration heats of pairs of ions may be determined experimentally, it is possible to split up the hydration heats of a pair into the separate contributions of cation, W_{M^+} , and anion, W_{X^-} :

$$H = -(W_{M^+} + W_{X^-}) \quad (2)$$

This problem has been studied by a number of investigators, who have produced consistent values for a number of monatomic ions. Individual ion hydration heats due to Latimer *et al.*¹ and due to Verwey² are shown in Table 1.

TABLE 1. HYDRATION HEATS OF IONS, kcal/g ION

Ion	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	F ⁻	Cl ⁻	Br ⁻	I ⁻
Latimer <i>et al.</i> ¹	121.2	94.6	75.8	69.2	62.0	122.6	88.7	81.4	72.1
Verwey ²	120	94.5	75	69	61	122	89.5	83	73.5

In the case of an unsymmetrical polyatomic anion such as benzenesulphonate, the hydration heat W_{X^-} cannot be derived from equations (1) and (2), since the lattice energy of a crystalline

¹ W. M. Latimer, K. S. Pitzer, and C. M. Slansky, *J. Chem. Phys.* 7, 108 (1939).

² E. J. W. Verwey, *Rec. Trav. Chim. Pays-Bas* 61, 127 (1942).