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ALKALOIDS FROM *ASPIDOSPERMA AUSTRALE* MÜLL. ARGOV.

RELATIONSHIP OF OLIVACINE TO *U*-ALKALOID C

Miguel A. Ondetti and Venancio Deulofeu

Laboratorios de Investigación, E. R. Squibb and Sons Argentina S. A.,
Av. Sir Alexander Fleming 1653, Martínez, Buenos Aires, Argentina

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From the bark (root) of *A. australe*, Müll. Argov. a plant which has a wide distribution in South America, we have isolated three alkaloids identical with other bases found in *A. ulei* Mgf. and *A. olivaceum* M. Arg., both growing in the same region.

The major alkaloid (alkaloid A), is a yellow base, $C_{17}H_{14}N_2$, $(\alpha)_D^{24°} \pm 0$, m.p. 314-316° (Kofler)[1]. Ultraviolet spectrum in ethanol and ethanol-hydrochloric acid, infrared spectrum and colour reactions in exact agreement with those of olivacine, an alkaloid isolated by Schmutz and Hunziker[2] from *A. olivaceum* (m.p. 318-324°; $(\alpha)_D^{25°} \pm 0°$) (Found: $C\text{-}CH_3$: 4.80; calc. 1 $C\text{-}CH_3$: 6.09).

The minor alkaloids are: Alkaloid B; $C_{18}H_{20}N_2$, m.p. 243-246°; $(\alpha)_D^{29°} + 112°$ (pyridine). Ultraviolet spectrum in ethanol and ethanol-hydrochloric acid, infrared spectrum and colour reactions identical

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[1] M.p. not corrected. Analytical figures satisfactory for the isolated products and new substances.

[2] Schmutz and Hunziker, *Pharm. Acta Helv.* 33, 341 (1958).

with those described for *u*-alkaloid C, isolated from *A. ulei* by the same authors[3] (m.p. 249-252°; $(\alpha)_D^{25^\circ}+ 112^\circ$).

Alkaloid C; $C_{18}H_{22}N_2$, m.p. 78-80° (Kofler); 118-121° (Capillar); $(\alpha)_D^{25^\circ}+ 11.5$; hydrochloride m.p. 240-241°; methiodide m.p. 204-206°. Ultraviolet spectrum m.p. and colour reactions identical with those of uleine from *A. ulei*[4] (m.p. 76-118°; Kofler); $(\alpha)_D^{25^\circ}+ 16^\circ$. (Hydrochloride m.p. 241-242°; methiodide m.p. 204-206°).

The base m.p. 314-316° (olivacine) gives a methiodide that decomposes at 320° and which was reduced with Adams' catalyst, in ethanol, to a base C18H20N2, m.p. 223-225°. It contains one N-methyl and two C-methyl groups (Found: $N{-}CH_3$, 5.35; $>C{-}CH_3$, 11.10; calc. 1 $N{-}CH_3$, 5.69; 2 $C{-}CH_3$: 11.38). This new base has colour reactions and an ultraviolet and infrared spectra in potassium bromide identical with the spectra of alkaloid B from *A. australe* (*u*-Alkaloid C from *A. ulei*) and appears to be the racemic form of it. This is supported by the fact that dehydrogenation of *u*-alkaloid C with platinum, in boiling diphenyl ether produces olivacine, identified by mixed m.p. and UV-spectrum.

The reduced base is identical with one isolated from the aerial bark of the same *Aspidosperma*, m.p. 223-225° $(\alpha)_D^{25^\circ} \pm 0^\circ$ (no depression in mixed m.p.; same colour reactions, UV- and IR-spectra).

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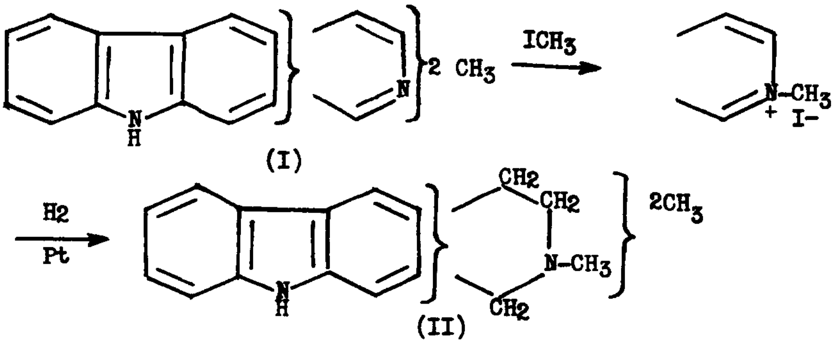
[3] Schmutz and Hunziker, *Helv. Chim. Acta* 41, 288 (1958).

[4] Schmutz, Hunziker and Hirt, *Helv. Chim. Acta* 40, 1189 (1957).

The aerial bark contains also olivacine and uleine.

Schmutz and Hunziker[3] have noted that the ultraviolet spectrum of u-alkaloid C, is almost identical with the spectrum of carbazol, except that it is displaced 5-6 mμ to longer wave lengths. It does not shift on the addition of hydrochloric acid, although the maxima are increased (hyperchromic effect). These properties are exactly those of the base obtained reducing olivacine methiodide, and of alkaloid B and the inactive base m.p. 223-225º from A. australe.

The easy reduction of the methiodide of olivacine, the presence of an N-methyl group in the reduction product (II) and the carbazol spectrum of the latter, are in agreement with the hypothesis that olivacine has a carbazol unit condensed with a pyridine ring, forming an indol-quinoline or an indol-isoquinoline structure. Although the indol-quinoline structure can not be excluded, the isoquinoline (I) is more acceptable on the basis of the UV-spectrum, because in the quinoline the nitrogen of the reduced base would be directly attached to the benzene ring of carbazol, and as pointed by Schmutz and Hunziker[3] a shift in the maxima could be expected, in passing from ethanol to ethanol-hydrochloric acid, which, however, does not happen.



(I)

(II)

Because of the value obtained for C-methyl in the reduction product, two C-methyls are also present in the molecule of olivacine. At least one methyl must be a substituent of the pyridine ring to explain the optical activity of u-alkaloid C.

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