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# THE STRUCTURE OF ANGUSTIFOLINE[*]

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Angustifoline ($C_{14}H_{22}ON_2$) is an alkaloid that has been isolated from three plants: *Lupinus angustifolius*, *L. polyphyllus* and *L. albus*.[3] It is a monoacidic base containing a lactamic carbonyl and a double bond. Both functions are indicated in the infrared spectrum and their presence confirmed by catalytic hydrogenation which in neutral solution gives dihydroangustifoline, $C_{14}H_{24}ON_2$, and in acid solution produces dihydrodesoxyangustifoline, $C_{14}H_{26}N_2$, a diacidic base.[4] Wiewiorowski, Galinovsky

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[3] M. Wiewiorowski and M.D. Bratek, *Bull. acad. polon. sci.* Kl II, **4**, 3 (1956).

[4] M. Wiewiorowski, F. Galinovsky and M.D. Bratek, *Monatsh.* **88**, 663 (1957).

and Bratek[4] who carried out preliminary work on the alkaloid concluded from chemical and spectral evidence that it contained a 1,2-disubstituted-piperid-6-one.

The present investigation has made it possible to arrive at the total structure of the alkaloid. According to the infrared and NMR spectra of angustifoline, the double bond must be present in a vinyl group, and the infrared spectrum of dihydroangustifoline no longer shows the bands characteristic of the vinyl group, while its NMR spectrum contains the signal typical of a methyl group (3.83 p.p.m.). The base must have a tricyclic structure.

The basic nitrogen is secondary and reacts with formic acid producing N-formylangustifoline, $C_{15}H_{22}O_2N_2$, m.p. 136°, which in the infrared contains bands at 1645 and 1675 $cm^{-1}$ attributable to the original lactamic carbonyl and to the new carbonyl group. On the other hand, angustifoline I reacts with a mixture of formic acid and formaldehyde in a different way. The reaction gives rise to a product IIb ($C_{15}H_{24}O_2N_2$) isomeric with the naturally-occurring 13-hydroxylupanine. The product melts at 190-191°, and its infrared absorption spectrum differs from that of 13-hydroxylupanine only in the region 1000-1100 $cm^{-1}$. Since these differences are the same as those observed between the spectra of 13-epihydroxysparteine[5] and 13-hydroxysparteine, it is assumed that IIb is 13-epihydroxylupanine. This conclusion finds confirmation in the catalytic hydrogenation of IIb which converts it into 13-epihydroxysparteine III, m.p. 171-172°, the infrared spectrum of which is identical with that published by Bohlmann *et al.*[5] who prepared this compound.

Dehydration of III with phosphorus pentoxide at 140° followed by hydrogenation over platinum gave (—)-sparteine (IV) which was characterized as the dipicrate, m.p. 206°, either alone or in admixture with an authentic specimen. The identity was also established by comparison of the X-ray powder pattern of the picrate of IV with that of (—)-sparteine dipicrate: they were superimposable.

The foregoing series of reactions makes it possible to assign to angustifoline the total structure I, and to represent the transformations as in the following scheme:

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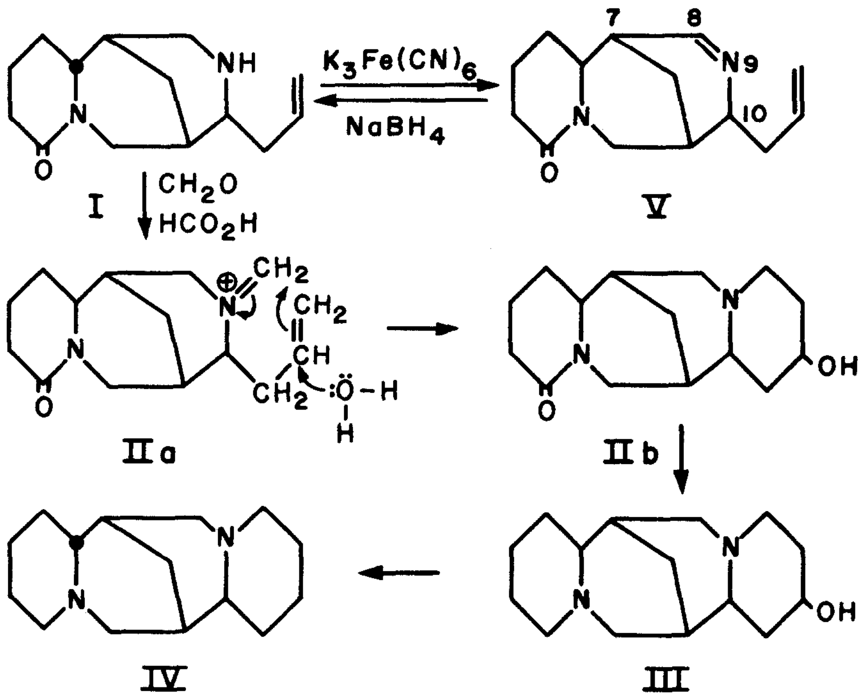
[5] F. Bohlmann, E. Winterfeldt and H. Brackel, *Chem. Ber.* **91**, 2194 (1958).



The anhydronium salt IIa of N-hydroxymethylangustifoline has not been isolated, although the presence of an intermediate is indicated on the paper chromatogram of the crude product of the reaction.

Oxidation of the alkaloid with potassium ferricyanide or with N-bromosuccinimide gives rise to dehydroangustifoline V ($C_{14}H_{20}ON_2$), m.p. 105°, which is converted back to angustifoline by the action of sodium borohydride or to dihydroangustifoline by catalytic hydrogenation. The perchlorate of dehydroangustifoline shows in the infrared a band at 1680 $cm^{-1}$ characteristic of an enamine salt. That the new double bond is at $C_8$ and not at $C_{10}$ is shown by the signals at -3.15 p.p.m. relative to tetramethylsilane in the NMR spectrum. With the double bond at $C_8$, the group $\underset{H}{>}C{=}N-$ is present and the signal of the H in this group would be expected to appear in that region somewhat analogous to an aldehyde H.[6]

Dehydroangustifoline V has been found to be identical with the alkaloid "w-102" isolated from L. angustifolius by Bratek and Wiewiorowski.[7]

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[6] G. van Dyke Tiers, Organic Section Exploratory NMR studies, Project 737602, Minnesota Mining and Manufacturing Compay.

[7] M.D. Bratek and M. Wiewiorowski, Roczniki Chem. **33**, 1187 (1959).