STUDY OF OXOAPHYLLIDINE

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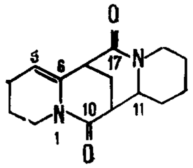
Previously [1] in a study of the oxidation of quinolizidine alkaloids of the sparteine series with potassium ferricyanide we found that a lactam carbonyl was formed in the molecule of an alkaloid of this type in the C_{17} position of the cis-quinolizidine nucleus.

In the present paper we give the results of a study of the oxidation of aphyllidine, which contains a double bond in the C_5–C_6 position of a trans-quinolizidine ring.

The oxidation was performed with potassium ferricyanide in an alkaline medium at room temperature. It was found that aphyllidine, with an isolated double bond in the molecule, was oxidized 1.5-2 times more slowly than pachycarpine, forming the corresponding C_{17}-oxo derivative.



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The compound, with the composition $C_{15}H_{20}N_2O_2$, corresponds to the oxoaphyllidine isolated [2] from Anabasis aphylla with mp 182-184°C, $[\alpha]_D^{20}$ −21°. The oxoaphyllidine (I) obtained by the oxidation of aphyllidine has mp 188-189°C, $[\alpha]_D^{20}$ −29.8° (c 0.56; ethanol). In the IR spectrum of (I) there is an absorption band at 1645 cm^{-1} corresponding to a lactam carbonyl, its area being twice as great as that of the corresponding signal for aphyllidine. Its UV spectrum: $\lambda_{max}^{C_2H_5}$ 244 nm (log ε 0.75). The mass spectrum of the substance had the peaks of the molecular ion, M^+ 260, and also peaks with m/e 150, 149, 203, and 231. The NMR spectrum contained the following signals: at 4.92 ppm due to an olefinic proton at C_5, a doublet at 4.62 ppm with an integral intensity corresponding to two protons (H_{2e} and H_{15e}); and a multiplet at 3.86 ppm corresponding to a tertiary proton at C_{11}.

The spectral characteristics presented and the results of a comparison of molecular rotation (ORD) curves of aphyllidine [3] and (I) at the extrema at 235-240 nm confirmed the structure of the latter. The hydrogenation of (I) in the presence of Raney nickel gave us dihydrooxoaphyllidine, $C_{15}H_{22}N_2O_2$, with mp 157-159°C, identical with oxoaphylline [2].

LITERATURE CITED

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