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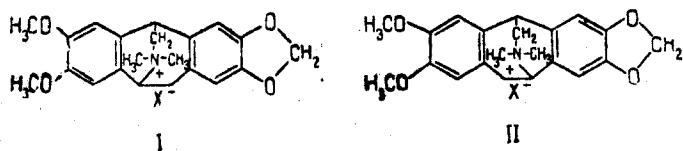
Khimiya Prirodnkh Soedinenii, Vol. 3, No. 1, pp. 68-69, 1967

We have previously reported the isolation from *Roemeria refracta* of a quaternary alkaloid roemrefine for which the pavine structure was proposed [1]. A two-stage Hofmann degradation has given a nitrogen-free substance with the composition $C_{19}H_{16}O_4$, mp 179-181°C. The UV spectrum of the first optically active des-base almost coincides with the spectrum of 1-des-iso-pavine [2], and differs substantially from the spectra of the 1-des-bases of alkaloids of the pavine series [3, 4]. The UV spectrum of the nitrogen-free product from roemrefine [λ_{\max} 247, 324 m μ (log ϵ 4.63, 4.10)] also differs from the IR spectra of the corresponding products from alkaloids of the pavine type [3, 4].

The oxidation of roemrefine with potassium permanganate in an aqueous medium gave m-hemipinic acid. The products of the oxidation were found to contain a second acid which had a similar R_f value on paper chromatography to hydrastic acid and 3,4-methylenedioxyphthalic acid. The production of m-hemipinic acid as almost the sole product of the oxidation also indicates the isopavine structure of roemrefine.

In the region of aromatic protons, the NMR spectrum of roemrefine has four equal singlets at δ 6.28, 6.67, 7.05, and 7.17, which shows the presence of substituents in positions 2, 3, 7, 8 of the aromatic rings. A $>N^+(CH_3)_2$ group appears in the form of two singlets at δ 3.38 and 2.9, the first value being normal for a methyl group on a quaternary nitrogen atom [5], but the second being considerably shifted to the high field region. On considering models of the isopavine and pavine structures, it can be seen that in the first case when two methyl groups are present on the nitrogen atom one of them is located above the plane of the benzene ring attached to the six-membered ring, which causes the above-mentioned shift of the signal of the methyl group. The protons of the methylenedioxy group are responsible for the appearance of two signals at δ 5.72 and 5.84. The considerable difference in the chemical shifts of the two protons of the methylenedioxy group is apparently due to the fact that the latter is present in the benzene ring attached to the six-membered ring. In this case, the difference in the environments of the two protons will be considerable. Thus, of the two possible structures for roemrefine, (I) and (II), the second is the most probable.

It is possible that roemrefine is a quaternary form of amurensinine, for which Santavi, et al. [6] have proposed an isopavine structure.



REFERENCES

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14 October 1966

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