A careful chromatographic investigation of the combined cardenolides from Evonymus medirossica Kloc., using the digitoxigenin L-arabinoside synthesized as a reference sample, showed that the glycoside is not present in the species of euonymus that we are investigating.

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THE STRUCTURE OF SPIREINE

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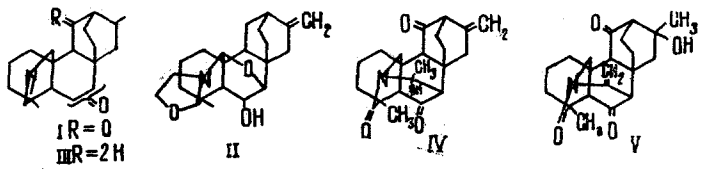
Khimiya Prirodnykh Soedinenii, Vol. 5, No. 5, p. 454, 1969

The isolation from Spireae japonica of a new alkaloid spireine $C_{22}H_{27}O_4N$ with mp 230° C (from ethanol) has been reported previously [1].

The molecular weight, determined mass-spectrometrically (M^+ ion, m/e 369), is in agreement with the empirical formula of spireine. The molecule of spireine contains two keto groups in unstrained rings (1727 cm^{-1}), a tertiary amide grouping (1683 cm^{-1}), and a tertiary hydroxyl group (3425 cm^{-1}), as is shown by a study of the IR spectra of spireine, its hydrochloride, and its dihydro and tetrahydro derivatives with the measurement of the integral intensities of the carbonyl bands.

The NMR spectra of spireine and its derivatives have shown the presence in its structure of two methyl groups on quaternary carbon atoms (1.44 and 1.49 ppm) and the groupings $CH_2{=}C\!\!<$ (4.81 and 4.97 ppm) and $-\overset{|}{C}-CH_2-N-C=O$ (δ_1 = 2.05 ppm; δ_2 = 2.47 ppm; J = 9.0 Hz. A study of the NMR and mass spectra of deuterated spireine and tetrahydrospireine shows the presence in it of three hydrogen atoms in $-\overset{|}{C}-\underset{|}{CH}-\underset{\|}{C}(O)-$, $-\overset{|}{C}-\underset{|}{CH}-\overset{|}{C}-$ or $-C(=O)-\underset{|}{CH}-\overset{|}{C}-$ groupings.

When spireine was heated with selenium at 340° C, a compound (I), $C_{20}H_{27}O_2N$, was obtained. Under similar conditions, Japanese authors [2] obtained compound III from the alkaloid (II) isolated from the same species of Spirea. On the basis of these results and also the IR, NMR, and mass spectra, the structure I may be put forward for the substance $C_{20}H_{27}O_2N$.



The results obtained permit two possible structures, IV and V, to be suggested for spireine.

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THE CONFIGURATION OF SOPHORIDINE

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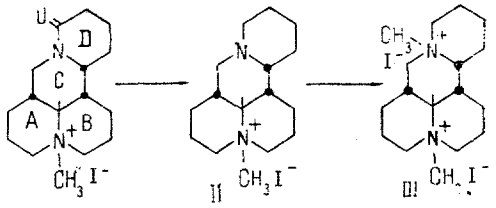
It has been shown previously [1] that in the lactam-containing alkaloid sophoridine [2, 3] the C/D rings are syn-cis-linked. To confirm this, the methiodide of sophoridine (I) was reduced with $LiAlH_4$. A product was obtained the methiodide of which was identical with the dimethiodide of sophoridane (III). Consequently, reduction given sophoridane monomethiodide (II) in which the free pair of the nitrogen atom of the trans-quinolizidine (A/B) system is blocked.



The IR spectra of I exhibits the band of a lactam carbonyl (1640 cm^{-1}) and lacks the band of a trans-quinolizidine system (2800–2700 cm^{-1}). The spectrum of II lacks the bands of both a lactam carbonyl and a trans-quinolizidine system, which indicates the cis-linkage of rings C/D in sophoridine.

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THE STRUCTURE OF BUCHARIDINE

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In the chromatographic separation of the combined alkaloids of Haplophyllum bucharicum Litv. we obtained a phenolic base with mp 251–252° C having the composition $C_{19}H_{25}O_4N$, mol. wt. 331 (mass spectrometry), and we have called it bucharidine.