ALKALOIDS OF Sophora alopecuroides

TRICROTONYLTETRAMINE

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From the fraction of strong bases from Sophora alopecuroides in the isolation of aloperine (the fraction soluble in petroleum ether) [1], together with the latter by fractional crystallization of the hydrochlorides we have isolated a base with the composition $C_{12}H_{24}N_4$, mp 101–103°C (anhydrous base from acetone, yield 0.0014%), which forms salts with two molecules of acid: a dihydrochloride $C_{12}H_{24}N_4 \cdot 2HCl$ with mp 289°C (decomp., from ethanol) and a dipicrate $C_{12}H_{24}N_4 \cdot 2C_6H_3N_3O_6$ with mp 222–224°C. Its molecular weight was confirmed by mass spectrometry (M^+ 224) and osmometrically (228.4). The presence of mobile hydrogens in the compound can be judged from the IR spectrum of the base (3250 and 3270 cm^{-1}) and also from the mass spectrum of the product of the replacement of the mobile hydrogen atoms by D with CH_3OD.

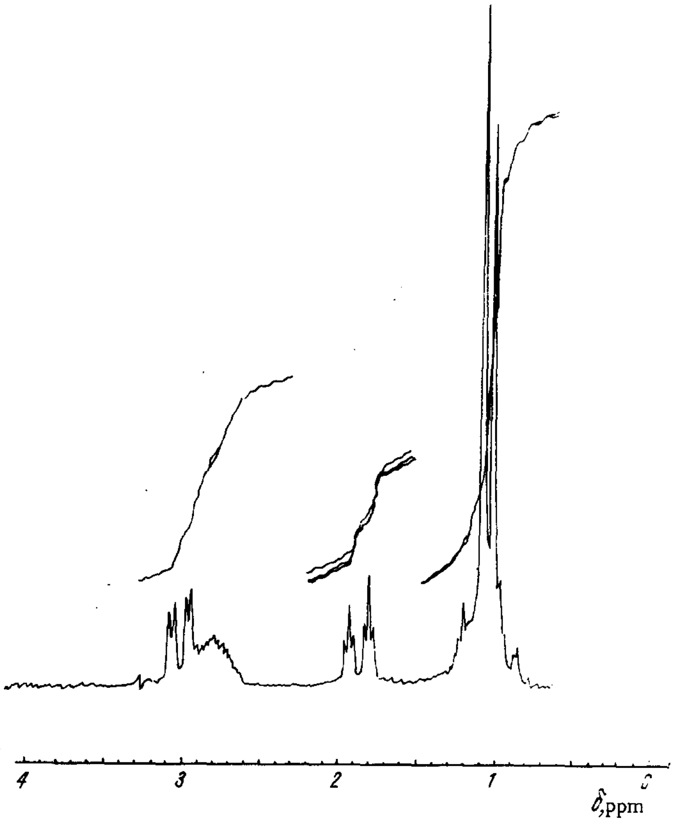


Fig. 1. NMR spectrum of tricrotonyltetramine.

All-Union Scientific-Research Institute of Medicinal Plants. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 752–754, November–December, 1974. Original article submitted August 17, 1973.

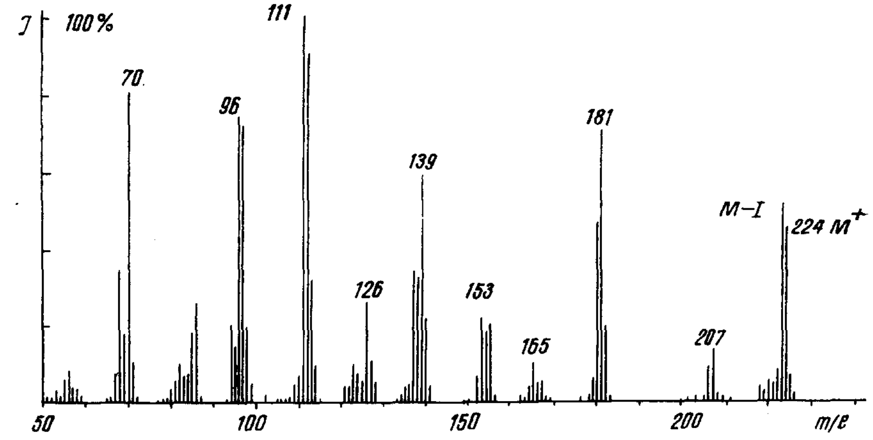
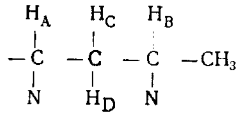


Fig. 2. Mass spectrum of tricrotonyltetramine.

The results of an analysis of the NMR spectrum (Fig. 1) using the INDOR method have shown that the molecule of the base contains the following structural fragment:



$$\begin{array}{cccc} H_A & H_C & H_B & \\ | & | & | & \\ -C & -C & -C & -CH_3 \\ | & | & | & \\ N & H_D & N & \end{array}$$

The signal of the mobile hydrogen apparently falls under the doublet from the methyl group (the intensity of all the signals in the range from 0.92-1.20 ppm corresponds to five proton units). No signals apart from those given above were observed in the NMR spectrum in the range from +17 to −10 ppm.

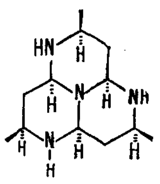
Thus, bearing in mind the molecular weight of the base it may be concluded that this fragment is repeated in the molecule three times with a symmetrical arrangement of all three units.

In a consideration of the partial formula it can be seen that the alkaloid is based on the imine of β-aminobutyraldehyde. However, the absence of the absorption of a C = N group in the IR spectrum and of the signal of a −N=CH proton in the NMR spectrum shows the cyclic nature of the molecule.

Of the three possible structural variants for this compound, on the basis of spectral characteristics, chemical correlations, and biogenetic considerations preference was given to the tricyclic derivative of formula (I).

In the mass spectrum (Fig. 2) of the compound there are the main peaks of the ions M^+ 224 (44%), M−1 (50%), M−17 (12%), M−43 (63%), M−17−42 (11%), 155 (20%), 153 (22%), 139 (57%), 111 (100%), 112 (90%), 96 (72%), 97 (70%), 70 (80%), the nature of the fragmentation under the action of electron impact agreeing well with the given formula of the base.

The presence of bands of trans protons to the unshared pair of electrons of the nitrogen atom in the IR spectrum of the compound (2820-2740 cm^{-1}) and also the existence of trans-diaxial spin−spin coupling constants (J_{BD} = 10 Hz, J_{AD} = 11 Hz) showed the equatorial arrangement of the methyl groups and the stereostructure of the compound.



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The base that we have isolated, which is known in the literature under the name of tricrotonyltetramine was first obtained by the reaction of crotonaldehyde, aldol, or aldehyde−ammonia with ammonia under severe conditions [2]. The constants of a synthetic sample (mp 96°C for the hydrate and 102°C for the anhydrous form) coincide with those of the base that we have isolated. Thus, in view of the conditions for the synthetic preparation of this substance and the mild conditions of its isolation from the plant, it may apparently be considered that it is not an artefact.

EXPERIMENTAL

The IR spectrum was taken on a UR-10 instrument, the mass spectrum on a Varian CH-8 instrument at a temperature of 20-30°C and an energy of the ionizing electrons of 70 eV, and the NMR spectrum on a Varian HA-100D instrument (in $CDCl_3$, 20°C, 0 — HMDS).

The melting point was determined on a Kofler block and the molecular weight in a Knauer osmometer. The analytical results corresponded to the calculated figures.

Isolation of the Alkaloid. Aloperine hydrochloride (technical, 2 g) was treated with 150 ml of ethanol, and the ethanol-insoluble residue consisted of tricrotonyltetramine hydrochloride (0.49 g or 0.0014%) with mp 289°C (decomp.). After two recrystallizations from acetone, the base melted at 95-96°C (hydrate) and 101-103°C (anhydrous form).

SUMMARY

From the fraction of strong bases of Sophora alopecuroides (flowering stage) a base $C_{12}H_{24}N_4$, mp 101-103°C, has been isolated which has been identified as tricrotonyltetramine. Its stereoconfiguration has been established.

LITERATURE CITED

1. T. E. Monakhova, O. N. Tolkachev, V. S. Kabanov, M. E. Perel'son, and N. F. Proskurnina, Khim. Prirodn. Soedin., 472 (1974).
2. M. Delépine, Compt. Rend., 216, 649, 785 (1943).