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STRUCTURE OF HERBOXINE

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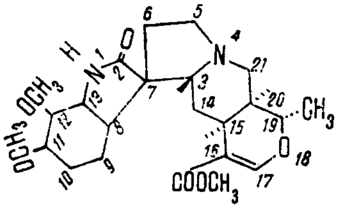
Continuing an investigation of the alkaloids of *Vinca herbaceae* [1], we have isolated a new base, which we have called herboxine. Herboxine (I), $C_{23}H_{28}N_2O_6$, has mp 179-181°C, $[\alpha]_D$ +40° (c 1.13; methanol). The UV spectrum of (I) — λ_{max} 224 nm (log ε 4.39), inflection at 250 nm — is characteristic for the hydroxyindole alkaloids.

The IR spectrum of (I) has absorption bands at 775 and 800 cm^{-1} (1,2,3,4-tetrasubstituted benzene ring) and 1710 and 1635 cm^{-1} (ester and amide carbonyl groups). The mass spectrum of (I) is characterized by the peaks of ions with m/e 428 (M^+; 100%), 413, 411, 397, 223, 222, 219, 208, 206, 204, 180, and 69. The NMR spectrum of (I) shows signals from the protons of a $>CH-CH_3$ group (δ 1.18 ppm, 3 H, doublet, J = 6 Hz; and 4.12 ppm, 1 H, quartet, J = 10 Hz), the methoxy of an ester group (3.37 ppm, singlet), two aromatic methoxyls (3.71, 3.78 ppm, singlets), $>C=CH-O-$ (7.32 ppm, 1 H, singlet), NH (8.20 ppm, 1 H, broadened singlet), and two aromatic protons, C_9H (6.70 ppm, 1 H, doublet, J = 8 Hz), and $C_{10}H$ (6.40 ppm, 1 H, doublet, J = 8 Hz).

The similarity of the IR, mass, and NMR spectra of herboxine and those of majdine (II) and isomajdine (III) [2] permitted the assumption that (I) is an isomer of majdine or isomajdine. To answer this question, we performed a comparative investigation of the chemical properties and spectral characteristics of majdine, isomajdine, and the products of their isomerization in acetic acid (IV and V, respectively) [3] with those of herboxine. It was found that herboxine was identical with compound (IV), i.e., (I) differs from majdine by the configuration at C_3 and has the structure



I

EXPERIMENTAL METHOD

The IR spectra were taken on a UR-20 spectrometer (tablets with KBr), the mass spectra on an MKh-1303 instrument with a glass inlet system at 40 eV, and the NMR spectra on a JNM 4H-100/100 Hz instrument with HMDS as internal standard (δ scale). The homogeneity of the substances was checked by chromatography in a thin layer of KSK silica gel in the ethyl acetate–methanol (9:1) system.

Herboxine (I). The material (12 g) from the mother liquor after the isolation of majdine was passed through a column of alumina (activity grade II, 1:10). Elution was per-

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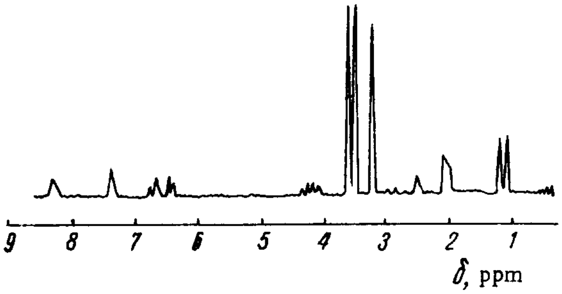

Fig. 1. NMR spectrum of herboxine.

with ether, ether—chloroform (1:1), and chloroform. On treatment with methanol, the chloroform fraction yielded (I) with mp 179-181°C (methanol), R_f 0.20.

Isomerization of Majdine. A solution of 0.5 g of majdine in 50 ml of 10% acetic acid was heated on the water bath for 10 h. After cooling, it was diluted with water, made alkaline with caustic soda, and extracted with chloroform. The chloroform was distilled off, and the residue (0.450 g), with R_f 0.2, 0.7, 0.8, and 0.85, was separated preparatively. This gave 0.1 g of (IV) with R_f 0.2; 0.05 g of (V) with R_f 0.7; 0.150 g of (II) with R_f 0.80; and 0.030 g of (III) with R_f 0.85.

The base (IV), $C_{23}H_{28}N_2O_6$; $[\alpha]_D$ +45° (c 1.3; methanol). IR spectrum, cm^{-1}: 775, 800 (1,2,3,4-tetrasubstituted benzene ring), 1710, 1640 (—CO—, NCO). Mass spectrum: 428 (M^+) (100%), 413, 411, 397, 224, 223, 222, 208, 206, 204, 190, 180, and 69. NMR spectrum: >CH—CH_3 (1.18 ppm, 3 H, doublet, J = 6 Hz; 4.10 ppm, 1 H, quartet, J = 10 Hz), $COOCH_3$ (3.39 ppm, 3 H, singlet), Ar—OCH_3 (3.47 ppm, 6 H, singlet), >C=CH—O— (7.30 ppm, 1 H, singlet), NH (8.29 ppm, 1 H, broadened singlet), C_9H (6.70 ppm, 1 H, doublet, J = 8 Hz), $C_{10}H$ (6.45 ppm, 1 H, doublet, J = 8 Hz).

The base (V), $C_{23}H_{28}N_2O_6$; $[\alpha]_D$ +28° (c 0.7; methanol). IR spectrum, cm^{-1}: 780, 805 (1,2,3,4-tetrasubstituted benzene ring), 1710, 1640 (CO, NCO), 3440 (NH). Mass spectrum: 428 M^+ (100%), 413, 411, 397, 224, 223, 222, 208, 206, 204, 190, 180, and 69. NMR spectrum: >CH—CH_3 (1.19 ppm, 3 H, doublet, J = 6 Hz; 4.15 ppm, 1 H, quartet, J = 10 Hz); $COOCH_3$ (3.60 ppm, 3 H, singlet); Ar—OCH_3 (3.85; 3.87 ppm, singlets), >C=CH—O— (7.35 ppm, 1 H, singlet), NH (7.75 ppm, 1 H, broadened singlet), C_9H (7.00 ppm, 1 H, doublet, J = 8 Hz), and $C_{10}H$ (6.45 ppm, 1 H, doublet, J = 8 Hz).

SUMMARY

A new hydroxyindole alkaloid has been isolated from the roots and epigeal part of *Vinca herbaceae* — herboxine, $C_{23}H_{28}N_2O_6$, $[\alpha]_D$ +40° (c 1.13; methanol).

On the basis of UV, IR, NMR, and mass spectroscopy and a transition from majdine to herboxine, structure (I) has been proposed for it which differs from that of majdine by the configuration at C_3.

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