ISOLATION FROM Vinca erecta OF VINERIDINE N-OXIDE AND 16-METHOXYVINCADIFFORMINE N-OXIDE

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Continuing the separation of the nonphenolic fraction of the chloroformic extract of the epigeal part of V. erecta (collected in the Tashkent oblast) [1] on a column of alumina, we have isolated three bases.

Base (I) with mp 193-195°C (chloroform), $[\alpha]_D$ +20° (c 0.68; methanol) is readily soluble in water and methanol and less readily in chloroform and acetone. IR spectrum (KBr): 1720 cm^{-1} ($COOCH_3$). The mass spectrum of (I) has the peaks of ions with m/e 412 (M^+) – 7%, 398 (M – 16) – 100, 243 – 9, 223 – 40, 208 – 9, 189 – 12, 69 – 26%. In the NMR spectrum of (I) (CD_3OD) there are the signals of the protons from $C_{10}H-CH_3$ (1.25 ppm, doublet, and 4.20 ppm, quartet), $COOCH_3$ (3.30 ppm, singlet), $Ar-OCH_3$ (3.75 ppm, singlet), and three aromatic protons (6.50-7.15 ppm).

The closeness of the IR and NMR spectra of (I) and of vineridine [1], and also the difference in the peaks of the molecular ions in the mass spectrum by 16 m/e permits the assumption that (I) is vineridine N-oxide. The reduction of (I) with Zn/HCl gave a product which was identified by its IR and mass spectra, its R_f values, and a mixed melting point as vineridine.

Base (II), with mp 150-152°C (acetone) is readily soluble in water and methanol. IR spectrum (KBr): 1680, 1650 cm^{-1} ($=C-COOCH_3$). Its mass spectrum: m/e 384 (M^+) – 4%, 368 (M – 16) – 26, 366 – 15, 338 – 12, 125 – 13, 124 – 100, 69 – 8%.

In the NMR spectrum of (II) ($CDCl_3$) there are the signals of the following protons: CH_2-CH_3 (0.62 ppm, 3H, triplet), $COOCH_3$, and $Ar-OCH_3$ (3.72 ppm, 6H, singlet).

The similarity of the IR and NMR spectra of (II) and of 16-methoxyvincadifformine [2], the difference in the peaks of the molecular ions by 16 m/e, and the identity of the other fragments permits the conclusion that (II) is 16-methoxyvincadifformine N-oxide. The reduction of (II) with Zn/HCl gave 16-methoxydihydrovincadifformine, and reduction with lithium tetrahydroaluminate gave 16-methoxyvincadifforminol (M^+ 342). The latter is also formed from ervincinine on reduction with lithium tetrahydroaluminate. The epoxide bond in ervincinine [3] was determined from a number of analogies with other alkaloids. The formation of methoxyvincadifforminol shows that the base contains a lactam carbonyl like ervinidinine and that ervincinine has the structure of 10-oxo-16-methoxyvincadifformine.

Base (III) was identified by its spectral and chemical properties as majdine [4]. When majdine was heated with 10% acetic acid, two new isomers of majdine were isolated: $C_{23}H_{28}N_2O_6$, $[\alpha]_D$ +45° (c 1.3; methanol) (IV) and $C_{23}H_{28}N_2O_6$, $[\alpha]_D$ +28° (c 0.7; methanol) (V).

The absence from the IR spectra of these isomers of the trans band at 2800 cm^{-1} and the positive Cotton effect at 250 μ in the ORD show that (IV) and (V) differ from majdine and isomajdine by the configuration at C_3. In the NMR spectra of (III) and (IV), the signals of the protons in the $C_{19}H-CH_3$ group appear, respectively, at 1.19 ppm, doublet, J = 6.5 Hz, and 4.11 ppm, quartet, J = 10 Hz. The similarity of the IR and mass spectra and the identity of the NMR spectra with the exception of the chemical shifts of the proton at C_9H, which is shifted downfield by 0.3 ppm in (V), leads to the conclusion that (IV) and (V) are spiro isomers at C_7 and the epiallo forms of majdine and isomajdine.

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