Chemistry

1965

SovietRxiv

structural formula of vinerine and vineridine

Figure 1: structural formula of vinerine and vineridine

Abstract

Full Text

Chemistry

Sh. Z. Kasymov, P. Kh. Yuldashev, Corresponding Member of the Academy of Sciences of the USSR S. Yu. Yunusov

The Structure of Vinerine and Vineridine

From the aerial part of *Vinca erecta* we isolated new alkaloids—vinerine-I and vineridine-II ([1]). Analysis of I and II, of their salts, and determination of the molecular weight established the composition $C_{22}H_{26}O_5N_2$. Both bases contain two methoxyl groups, one of which is present as an ester group, and the other in the benzene ring.

On acetylation with acetic anhydride, vinerine and vineridine form identical acetyl derivatives $C_{24}H_{28}O_6N_2$, m.p. 158-159°, $(\alpha)_D^{20} = -99.5$ ($C = 1.9$; acetone). The UV spectrum has three maxima: 212, 240, and 286 ($\log \varepsilon$ 4.68; 4.40; 3.98).

The IR spectrum contains bands at 1765 and 1640 cm^{-1} ($H_3COOC-\overset{|}{C}=\overset{|}{C}-O-C \equiv$), 1700 cm^{-1} (amide carbonyl), and the band of an N-H group is absent. On heating with alcoholic alkali, vinerine gives an amorphous amino acid; methylation of this with diazomethane gave the original base. Comparison of the mass spectra of vinerine and vineridine with mitraphylline and carapanaubine ([2]) established that I and II belong to the oxindole alkaloids. Comparison of the NMR spectra of reserpinine and N-acetylvinerine reveals the position of the methoxyl group in the benzene ring at the C-11 atom. On boiling vineridine in pyridine for five hours, vinerine was obtained; in this process a change in configuration occurs at the C-4 atom, characteristic of oxindole alkaloids ([3]). On the basis of these data, vinerine and vineridine have the structure:

For identification, treatment of reserpinine with lead tetraacetate ([4]) gave acetoxyreserpinine $C_{24}H_{28}O_5N_2$, m.p. 206-207°, $(\alpha)_D^{18} = +125.2$ ($C = 1.11$, chloroform). The UV spectrum has two maxima: 236; 284 ($\log \varepsilon$ 4.30; 3.42), and the IR spectra have bands at 1760 cm^{-1} ($O-CO-CH_3$), 1720 and 1640 cm^{-1} ($H_3COOC-\overset{|}{C}=\overset{|}{C}-O=C$), and the band of an NH group is absent.

Isomerization of acetoxyreserpinine in an acidic medium gave oxindolereserpi-

nine, m.p. 200–201°, which proved not to be identical with vinerine and vineridine. The UV and IR spectra of oxindolereserpinine, I, and II are similar; consequently, they are stereoisomers. Taking into account the α-orientation of the C-15 atom in heteroyohimbine ([5]) and oxindole alkaloids, in vinerine and vineridine the configuration of atoms C-19 and C-20 remains unresolved.

Institute of the Chemistry of Plant Substances
Academy of Sciences of the Uzbek SSR

Received
6 March 1965

References

1. Sh. Z. Kasymov, P. Kh. Yuldashev, S. Yu. Yunusov, *Dokl. Akad. Nauk SSSR*, **162**, No. 1 (1965).

2. V. Gilbert, J. A. Brissolese et al., *J. Am. Chem. Soc.*, **85**, 1523 (1963).

3. J. C. Seaton, M. D. Nair et al., *Canad. J. Chem.*, **38**, 1035 (1960).

4. N. Finch, C. W. Gemenden et al., *J. Am. Chem. Soc.*, **85**, 1520 (1963).

5. M. Shamma, J. M. Richey, *J. Am. Chem. Soc.*, **85**, 2507 (1963).

Note: Figure translations are in progress. See original paper for figures.