Reports of the Academy of Sciences of the USSR

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Sciences of the USSR S. Yu. Yunusov

1965

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1965. Volume 163, No. 1

Chemistry

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The Structure of Vincarine

Vincarine —$C_{21}H_{26}O_3N_2$ —was isolated from the roots of *V. erecta* (^{1}). Determination of the molecular weight by mass spectrometry refined the empirical composition to $C_{21}H_{24}O_3N_2$. Study of the NMR spectra of vincarine and its O,N-diacetate established the presence of an ester, an ethylidene, and a secondary alcoholic group.

The UV spectrum of vincarine has two maxima, $\lambda_{\max}$: 242 and 292 ($\log\varepsilon$ 3.84, 3.50), characteristic of alkaloids that are indoline derivatives (^{2}). In the UV spectrum of O,N-diacetylvincarine, four maxima, $\lambda_{\max}$, are observed: 210, 250, 280, and 290 ($\log\varepsilon$ 4.30, 4.09, 3.45, and 3.30), characteristic of N-acylindoline derivatives (^{3}). Reduction of O,N-diacetylvincarine with sodium borohydride results in acetolysis with formation of O-acetylvincarine, m.p. 56–57°, whose UV spectrum has two maxima, $\lambda_{\max}$, 244 and 293 ($\log\varepsilon$ 3.82, 3.38). In the IR spectrum of O-acetylvincarine there is an intense band at 1740 cm^{-1}, corresponding to two ester groups. In the mass spectra of vincarine and its O,N-diacetate, intense peaks of the molecular ions 352 and 436 m/e are observed, confirming the composition of the alkaloid. In the mass spectrum of vincarine there are ions of the indole part of the molecule: 130, 143 m/e, and of the non-indole part: 190 and 222 m/e. The ions 130 and 222 m/e make up the mass of the molecular ion, 352 m/e. The mass spectrum of O,N-diacetylvincarine has peaks: 130, 143, 190, 222, 264, 377, and 436 m/e. The ion 377 m/e is formed by cleavage of an acetoxy group from O,N-diacetylvincarine. The ion 264 m/e must be formed from that part of the molecule which contains the acetoxy group, since the acetyl group at the secondary nitrogen atom is readily cleaved off during mass spectrometry. Thus, the masses 42, 130, and 264 make up the molecular ion —436 m/e —of O,N-diacetylvincarine.

Comparison of the mass spectrum of vincarine with the spectrum of the alkaloid quebrachidine (^{4}) established their identity. However, the properties of quebrachidine and vincarine are different. Therefore vincarine is possibly a stereoisomer of quebrachidine.

chemical structure

Figure 1: chemical structure

On oxidation of vincarine with lead tetraacetate, an indole base was obtained, m.p. 159-160°, in whose IR spectrum there are bands of an ester carbonyl at 1755 cm^{-1}, an aldehyde at 1710 cm^{-1}, and a secondary nitrogen atom at 3400 cm^{-1}. On reduction of the indole base with sodium borohydride, a base was isolated, m.p. 241-242°, which forms an O-acetyl derivative, m.p. 272-274°.

The UV and IR spectra and other properties of the base, m.p. 241-242°, coincide with the properties of the alkaloid polyneuridine (5). The conversion to polyneuridine proved the structure of vincarine.

In quebrachidine the hydroxyl and ester groups occupy a cis arrangement, whereas in vincarine they must occupy a trans arrangement, since in the IR spectrum of vincarinic acid there are bands of an ionic carboxyl at 1600 cm^{-1} and of the deformation vibration of the NH_2 group at 1660 cm^{-1}, owing to formation of an inner salt. The indicated frequencies are characteristic of amino acids with a secondary nitrogen atom (6). Therefore the carbomethoxy group in vincarine is located close to the secondary nitrogen atom and lies in the same plane with it.

Thus, vincarine differs from quebrachidine in the configuration of the carbon atom C_{16}, is its diastereoisomer, and has the following structure:

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Received
18 I 1965

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