Chemistry

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1964

SovietRxiv

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Abstract

Full Text

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Vincarine—a New Alkaloid from the Roots of *Vinca erecta* Rgl. et Schmalh

In previous communications it was indicated that vincanine, vincanidine, and reserpinine had been isolated from the total alkaloids of *V. erecta* ([1,2]). Continuing the separation of the remaining part of the total alkaloids, we isolated a crystalline base with m.p. 263-264°, $(\alpha)_D + 13.98^\circ$ (methanol), (0.012% of the weight of the dry roots). On a thin layer of alumina and gypsum (9 : 1), in the ethyl acetate : methanol (8 : 2) system, $R_f = 0.55$. Elemental analysis of the base established its composition as $C_{21}H_{26}O_3N_2$. The alkaloid proved to be new and was named vincarine. Vincarine contains one methoxy group and two active hydrogen atoms.

Fig. 1. UV spectrum of vincarine (1) (0.0197 mg/ml), vincarine acid (2) (0.02 mg/ml), deoxyhexahydrovincanine (3) (0.04 mg/ml)

The IR spectra of the base show the presence of OH or NH groups (3335 cm^{-1}), a tertiary hydroxyl (1060 cm^{-1}); and an ester carbonyl—in the form of a carbomethoxy group (1733-1250 cm^{-1}). Vincarine is a derivative of *o*-disubstituted benzene (770 cm^{-1}). Kuhn-Roth oxidation revealed the presence of one C-alkyl group (3,4). Acetylation of vincarine gave an ON-diacetyl derivative, m.p. 170-171. On thin-layer chromatography in the ethyl acetate : methanol (9 : 1) system, $R_f = 0.60$.

In the IR spectrum of O,N-diacetylvincarine, lines appear that are characteristic of the $= N—CO—CH_3$ group at 1680 cm^{-1} and the $O—CO—CH_3$ group at 1765 cm^{-1}. Vincarine is not reduced, according to Adams, in alcohol or in glacial acetic acid; therefore it does not contain a double bond. On the basis of the data obtained, vincarine has the expanded formula:

$$C_{19}H_{21}(= N—H)(= N—)(COOCH_3)(OH).$$

The UV spectrum of vincarine has two maxima, λ (mμ): 242 (log ε 3.84) and 292 (log ε 3.50); the character of the absorption curves shows that it is an indoline derivative ([5]).

Figure 1 gives a comparison of vincarine with deoxyhexahydrovincanine. The ester group of vincarine, when heated in an evacuated sealed ampoule at 115° for 4 hr, is partially saponified, giving an amino acid with m.p. 289-290°, of composition $C_{20}H_{24}O_3N_2$. The UV spectrum has two maxima, λ (mμ): 242 (log ε 3.98) and 292 (log ε 3.65) (Fig. 1).

Vincaric acid is also formed when the base is saponified with 20% alcoholic alkali on a water bath for 3 hr. In the IR spectrum of vincaric acid there are frequencies of the ionic carboxyl at 1600 cm^{-1} and a deformation vibration of the group (1660 cm^{-1}) owing to the formation of intr

internal salt. The indicated frequencies are characteristic of amino acids with a secondary nitrogen atom ([6]). These data indicate the close proximity of the carboxyl group to the secondary nitrogen atom $N(a)$, located in the same plane with it. The tertiary hydroxyl group must, in this case, be located at the same carbon atom at which the carbomethoxy group is located.

[Displayed structural formula]

The carbomethoxy group is in the trans position with respect to the hydrogen atom at C_2; hence it becomes understandable that vincarine is saponified with difficulty, and also that vincarinic acid is not methylated by diazomethane or by methyl alcohol in the presence of hydrochloric or sulfuric acids.

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Received
28 IX 1963

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