

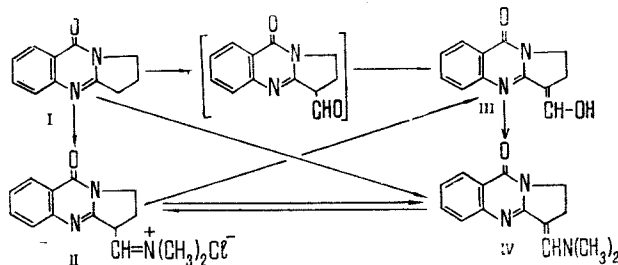
QUINAZOLINES.

IX. 3-HYDROXYMETHYLENE- AND 3-DIMETHYLAMINOMETHYLENEDEOXY-VASICINONES

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In order to synthesize 6-formyldeoxyvasicinone and investigate its chemical reactions, we have studied the formylation of deoxyvasicinone (I) by the Vilsmeier-Haack method. The formylation of aromatic and heterocyclic compounds takes place with the replacement of one of the hydrogen atoms of the aromatic ring by a formyl group [1]. There is information on the formylation of the side chain of condensed lactams [2]. The reaction of (I) with a mixture of phosphoryl chloride and dimethylformamide formed the product of formylation of the carbon atom in position 3 - 3-hydroxymethylenedeoxyvasicinone (III) or 3-dimethylaminomethylenedeoxyvasicinone (IV), depending on the conditions of working up the reaction mixture. Compound (III) was obtained when the reaction mixture was treated with a saturated solution of sodium acetate and (IV) when it was treated with a concentrated solution of ammonia.



The occurrence of the reaction in this direction is apparently explained by the activity of the hydrogen of the methylene group in position 3. Deoxyvasicinone reacts with benzaldehyde to form benzylidenedeoxyvasicinone [3]. Moreover, when (I) is brominated the hydrogen atoms at C₃ are replaced [4].

TABLE 1

Initial compound	Reaction product	Yield, %	mp, °C; solvent for recrystallization	R _f [Silufol, chloroform-methanol (10:1) system]
I + dimethylformamide + POCl ₃	II	73	285-287 (acetic acid)	0.62
II + CH ₃ COONa	III	68	205-206 (acetone)	0.48
I + dimethylformamide + POCl ₃ (aqueous NH ₃)	IV	65	177-179 (acetone)	0.68
II + aqueous NH ₃	IV	93	177-179 (acetone)	0.68
III + (CH ₃) ₂ NH	IV	97	177-178 (acetone)	0.67
IV + HCl	II	96	284-286 (acetic acid)	0.62

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Compounds (III) and (IV) are formed through an intermediate immonium salt (II) which it is possible to isolate in the individual state. Compound (III) is converted into (IV) even when it is mixed with an aqueous solution of dimethylamine at room temperature.

The structures of the compounds obtained were shown by the results of elementary analysis and by IR, PMR, and mass spectroscopy. The IR spectra of (III) had absorption bands at 1650 cm^{-1} ($\nu\text{C=O}$) and $3350\text{--}3600\text{ cm}^{-1}$ (νOH). The existence of compound (III) in the enolic form was confirmed by a qualitative reaction with ferric chloride. The PMR spectrum (IV) had the signals of the protons of a N-dimethyl group at 2.58 ppm (6 H, singlet), of two methylene groups at 2.60 ppm (2 H, triplet) and 3.90 (2 H, triplet), and of an aromatic ring at 7.02–7.58 ppm (3 H, multiplet) and 8.03 ppm (1 H, doublet). The signals of an olefinic proton appeared in the 7.35-ppm region. The PMR spectrum of (III) contains the signals of the protons of two methylene groups at 2.85 and 3.96 ppm and of an aromatic ring in the 7.15–7.80 and 8.49 ppm regions. The mass spectrum of (III) was characterized by the presence of ions with m/e 214 (M^+) and 185 ($\text{M} - \text{CHO}$), and that of (IV) by an ion with m/e 241 (M^+).

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EPIMACRONINE FROM *Ungermia spiralis*

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We have studied the bulbs of *Ungermia spiralis* gathered on May 25, 1974, in the Kara-Kala region of the Turkmen SSR. They have not been investigated previously.

The alkaloids were extracted by the usual method. From the mixture of bases were isolated lycorine (0.36% of the weight of the dry plant), tazettine, hippeastrine [1], and a new base (I).

Alkaloid (I) had mp $104\text{--}105^\circ\text{C}$, composition $\text{C}_{18}\text{H}_{19}\text{NO}_5$, M^+ 329, $[\alpha]_D^{+109}$ (c 0.72; chloroform), R_f 0.74 in the benzene-methanol (4:1) system in a thin layer of silica gel. UV spectrum of (I), λ_{max} , nm: 232, 272, 312 ($\log \epsilon$ 4.67, 3.99, 3.94). IR spectrum of (I), λ_{max} , cm^{-1} : 1715 ($>\text{C=O}$), 162 ($>\text{C=C}<$), 1500, 1480, 1440 (aromatic ring).

The NMR spectrum of (I) (CDCl_3 , JNM-4H-100 MHz instrument, HMDS, τ scale) had the following signals (ppm): singlets at 2.49 and 3.17 (aromatic protons at C_9 and C_{12}), 4.02 (2 H, $-\text{O}-\text{CH}_2\text{O}$), 6.60 (3H, $-\text{OCH}_3$), and 7.53 (3 H, $>\text{N}-\text{CH}_3$), and one-proton doublets from two olefinic protons at 3.8 and 4.67 ($J = 11\text{ Hz}$) for the protons at C_2 and C_1 , respectively.

A comparison of the characteristics given with those of macronine [2] and of synthetic epimacronine [3, 4] shows that (I) is epimacronine and this is the first time that it has been isolated from plants.

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