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ALKALOIDS OF *Fumaria vaillantii*. THE STRUCTURE OF NORJUZIPHINE

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Continuing the separation of the combined alkaloids of *Fumaria vaillantii* [1] collected in the Tashkent province in the period of flowering and incipient budding, in addition to the alkaloids mentioned previously we have isolated cheilanthifoline [2], parfumine [3], and d-stylopine [4], which were identified by direct comparison with authentic samples.

Base (I) with the composition $C_{20}H_{20}NO_4$, mp 264-266°C (chloroform–methanol), $[\alpha]_D$ −121.2° (c 0.28; methanol). The IR spectrum of (I) showed absorption bands at (cm^{-1}) 920, 940, 1045 (CH_2O_2), 1510 (aromatic ring), and 3150-3650 (OH). The UV spectrum of the base had two maxima, at 244 and 294 nm (log ε 3.90, 3.88). The NMR spectrum showed signals in the form of a three-proton singlet at 2.63 ppm from a N-CH_3 group and a four-proton singlet at 5.58 ppm from two methylenedioxy groups. The signals of aromatic protons appeared at 6.34 ppm (1 H) and 6.49 ppm (3 H).

The mass spectrum of the base lacked the peak of the molecular ion and showed peaks of ions with m/e 323, 174, and 148 (100%). The facts given above permitted base (I) to be identified as stylopine methohydroxide [5].

From the combined phenolic bases we isolated compound (II) with mp 198-199°C, $[\alpha]_D$ −18° (c 0.17; CH_3OH).

The UV spectrum of (II) had two maxima, at 228 and 285 nm (log ε 4.20, 3.56). The IR spectrum showed absorption bands at 3370 cm^{-1} (OH) and 1590 and 1610 cm^{-1} (aromatic ring). The mass spectrum of the base showed the peak of the molecular ion with m/e 285, and also the peaks of ions with m/e 178 (100%), 163, and 107. The NMR spectrum of the base recorded in methanol contained signals in the form of a three-proton singlet from a methoxy group at 3.79 ppm. In the aromatic region there were two two-proton doublets at 7.05 and 6.50 ppm (J = 8 Hz) from two pairs of equivalent ortho aromatic protons, and two one-proton doublets at 6.72 and 6.69 ppm (J = 8 Hz). Methylene protons appeared in the form of multiplets in the 2.50-2.90 ppm region.

At 4.19 ppm there was a one-proton quartet characteristic for the C_1 proton of a C_8-substituted benzyltetrahydroisoquinoline alkaloid [6]. According to the results of UV, IR, NMR, and mass spectroscopy, base (II) was a benzyltetrahydroisoquinoline alkaloid with methoxy and hydroxy groups in the isoquinoline moiety and a hydroxy group in the benzyl moiety of the molecule at C_4' [7]. When compound (II) was methylated by Craig's method [8] an N-methyl derivative was obtained which proved to be identical with juziphine (III) [6] according to TLC and a mixed melting point. Thus, the base (II) is norjuziphine

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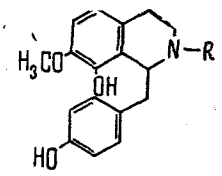

II. R=H
III. R=CH3

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SIMPLIFICATION OF THE METHOD OF ACTIVATING POLYSACCHARIDE SUPPORTS WITH CYANOGEN BROMIDE

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UDC 543.544

The method of activating polysaccharide supports by treatment with cyanogen bromide in an alkaline medium in order to obtain proteins or ligands for the biospecific (affinity) isolation of enzymes has come into wide use in laboratory and industrial practice [1, 2]. When using this method under laboratory conditions, the greatest difficulties arise in the preparation of crystalline cyanogen bromide, since the difficultly accessible cyanides of alkali metals are necessary [3, 4].

We have found that the difficulties connected with the use of cyanides and the preparation of crystalline cyanogen bromide can be circumvented if, in the first place, instead of cyanides the more accessible alkali metal thiocyanates are used [5]. The bromination of thiocyanates corresponds to the following equation:

$$SCN^- + 4Br_2 + 4H_2O \rightarrow CNBr + SO_4^{-2} + 8H^+ + 7Br^-$$

and the yields of cyanogen bromide determined by the iodometric titration of the solution formed as the result of the reaction amount to ~50%. In the second place, the distillation of the cyanogen bromide and the subsequent manipulations with it (storage, taking weighed samples, dissolution) can be excluded, since the solution of cyanogen bromide formed in its production can be used for activation. Since this solution still contains a considerable amount of acid in addition to cyanogen bromide, the activation process takes place in this case with a high consumption of alkali. Thus, a solution of cyanogen bromide obtained by the following method has been used to activate 30 ml of Sepharose gel swollen in water.

With cooling and stirring, a solution of 2 g of potassium thiocyanate [ch.d.a. ("pure for analysis") grade] in 15 ml of water was added dropwise to a mixture of 4 ml of bromine and 1 ml of water. The resulting solution of cyanogen bromide (~10 mM) with a pale yellow color and a slight deposit of salts, was combined with a suspension of Sepharose (30 ml of gel in 70 ml of water), and with cooling and stirring the mixture was brought to pH 10-11 with a 10 M solution of NaOH and was kept under these conditions for 15-20 min by the addition of a 4 M solution of NaOH. Then the suspension of activated gel was filtered off on

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