STRUCTURE OF CROCIFLORINONE

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Continuing an investigation of the alkaloids of the epigeal parts of Colchicum kesselringii Rgl. (synonym Colchicum crociflorum Rgl) collected in the Syrdar'ya region in the fruit-bearing period, we have isolated 0.50% of combined alkaloids. By separating them according to their basic strength and by chromatographing the fraction comprising the strong bases of nonphenolic nature on a column we have isolated, in addition to compounds mentioned previously [1-3], a new base which we have called crociflorinone.

Crociflorinone has the composition $C_{20}H_{25}O_3N$, mp 246-248°C (from acetone and ether), mol. wt. 329 (mass spectrometrically), methiodide with mp 271-272°C (from acetone). Its UV spectrum has inflections at 227, 276, and 288 nm. It can be seen from the IR spectrum of the base that it contains a carbonyl groups conjugated with a double bond (1695 cm^{-1}), and aromatic nucleus (1600, 900-800 cm^{-1}), and methylene groups (2940, 1470 cm^{-1}). From its mass-spectrometric decomposition [M^+, $(M-43)^+$, $(M-1)^+$ and other ions], crociflorinone can be assigned to the tetrahydroisoquinoline alkaloids containing a N-methyl group [4-6].

The NMR spectrum of crociflorinone methiodide (in CF_3COOH) shows the following signals (Fig. 1, δ scale): three-proton singlets at 2.65 and 3.02 ppm – two N-methyl groups; a six-proton singlet at 3.52 ppm – two O-methyl groups in an aromatic ring; a one-proton singlet at 6.48 ppm, due to the proton of an aromatic ring; and the doublets of two olefinic protons with their centers at 5.89 and 6.89 ppm. The presence of an AB quartet of olefinic protons and the location of one of the signals in the weak-field region of the spectrum shows that the crociflorinone molecule contains the fragment $-CH=CH-\overset{|}{C}=O$.

The facts given show the closeness of the structure of crociflorinone to partially hydrogenated homoproaporphine compounds of the type of bulbocodine [5] isolated from individual species of the family Liliaceae. It may have a structure with an olefinic bond at $C_{12}-C_{13}$ or at C_9-C_{10}.

The structure of 1,2-dimethoxy-9,10-dihydrohomoproaporphine has been confirmed for crociflorinone; according to a mixed melting point, it was identical with the O-methyl ether of jolanthamine, which we obtained from jolanthamine [8] with diazomethane.

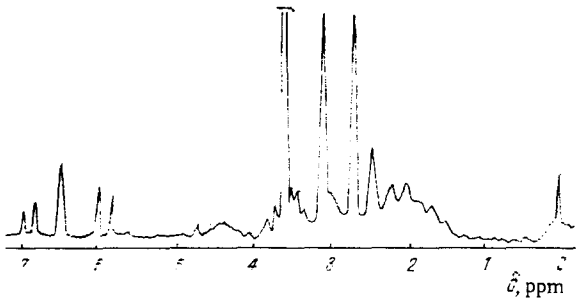

Fig. 1. NMR spectrum of crociflorinone (in CF_3COOH).

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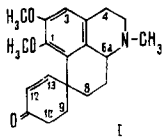
On the basis of the analogy with bulbocodine and jolanthamine it may be concluded that crociflorinone has the R configuration at the C_{6a} atom.



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