STRUCTURE OF KESSELRIDINE

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The present paper reports the structure of kesselridine – one of the new bases of the epigeal part of Colchicum kesselringii Rgl. [1, 2].

Kesselridine has the composition $C_{18}H_{23}O_4N$, mp 232-234°C, and $[\alpha]_D$ −50° (in pyridine), M^+ 317. Its UV spectrum (Fig. 1) has absorption maxima at 219 and 290 nm. Its IR spectrum (Fig. 2) has the absorption band of hydroxy groups (3230-3420, 3590 cm^{-1}) and of the C=C bonds of an aromatic ring (1595 cm^{-1}).

The NMR spectrum of kesselridine (Fig. 3) has the resonance signals of one N-methyl group (3.10 ppm) and one aromatic proton (6.68 ppm). Thus, kesselridine lacks the oxygen groups such as methoxy, carbonyl, and methylenedioxy groups, that are so characteristic for the colchicine alkaloids.

To establish the structure of kesselridine and the functions and positions of the substituents, we used the mass spectrometric method.

The presence in the mass spectrum (Fig. 4) of the base of the main ions $(M-1)^+$ and $(M-43)^+$ shows that it belongs to the tetrahydroisoquinoline derivatives containing an N-methyl group [3-5], the intensity of the peak of the molecular ion being approximately half that of the maximum ion $(M-1)^+$. According to the literature [3-5], such spectra are characteristic for the homoproaporphine alkaloids.

This is confirmed by the presence in the spectrum of kesselridine of peaks of ions with m/e 230 and 228. On the basis of biogenetic schemes, the aromatic proton in this base may be located at the C_3 atom, and then the ions mentioned can be assigned to the only possible structures [(I) and (II), respectively, in Scheme I].

The presence of ions with m/e 230 and 228 simultaneously excludes an aporphine skeleton. The peak of the molecular ion of the product of the methylation of kesselridine with diazomethane – O-methylkesselridine – corresponds to a mass number of 331. Furthermore, the ions of O-methylkesselridine cor-

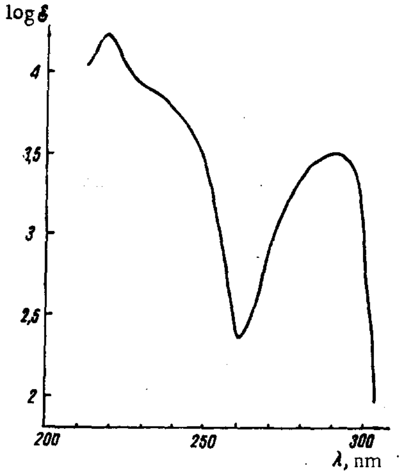

Fig. 1. UV spectrum of kesselridine.

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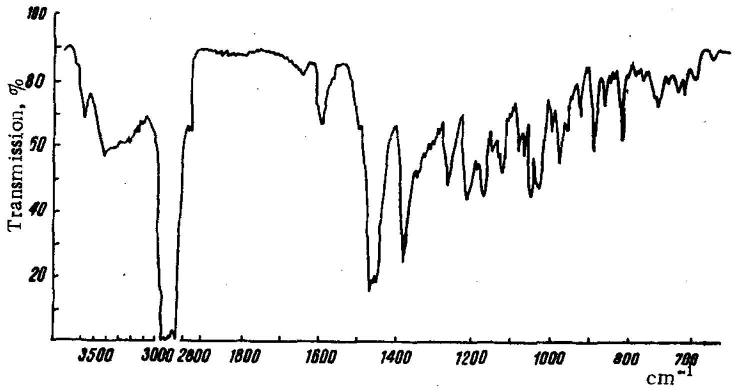


Fig. 2. IR spectrum of kesselridine.

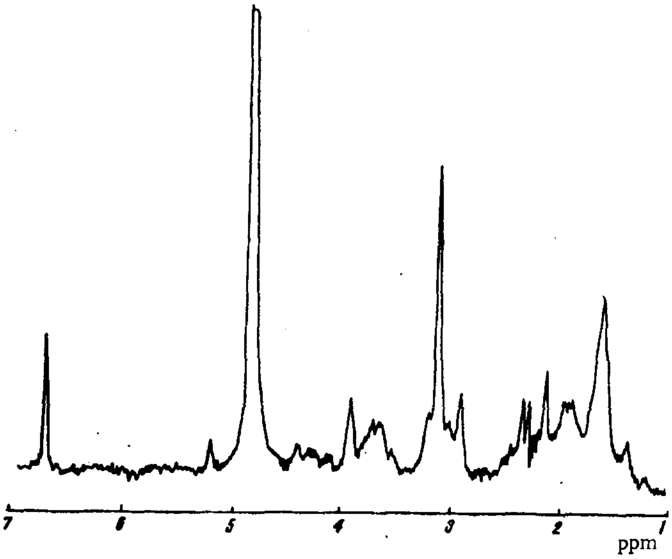


Fig. 3. NMR spectrum of kesselridine hydrochloride (in D_2O).

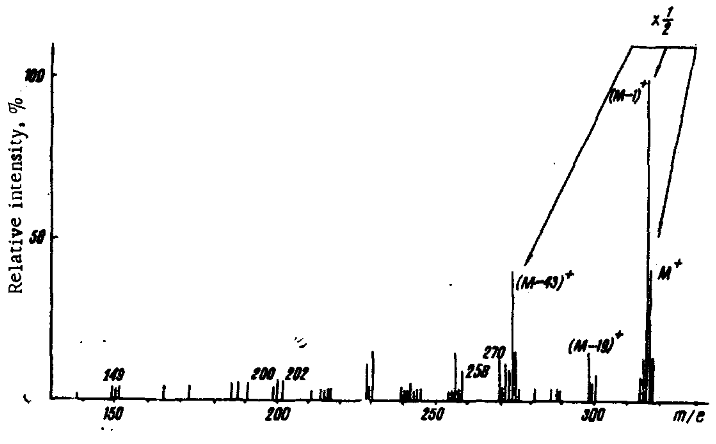
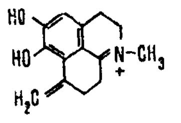
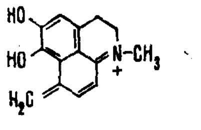


Fig. 4. Mass spectrum of kesselridine.

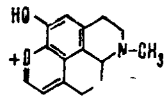
responding to the ions of kesselridine with m/e 230 and 228 are shifted by only 14, and not by 28 units. Consequently, one of the phenolic hydroxyls in the ions with m/e 230 and 228 is formed under the conditions of mass spectrometry by the cleavage of an ether bridge. The presence of an ether bridge in the fourth ring E is confirmed by the ion with m/e 242 (III).



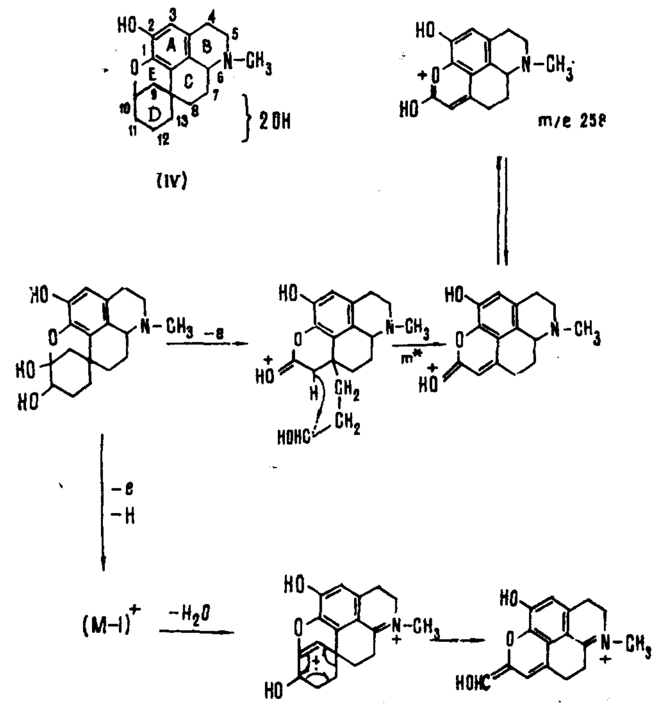
m/e 230 (I)



m/e 228 (II)



m/e 242 (III)



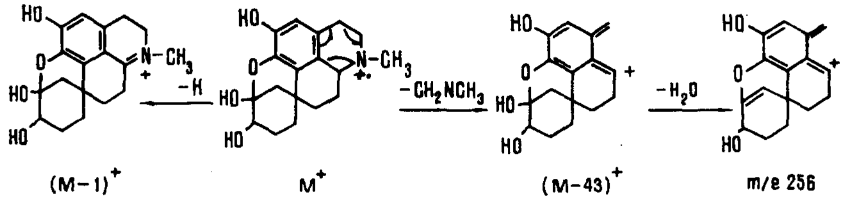
The nature of ring D is unambiguously determined by the combination of a number of factors. The ion with m/e 242 is formed by the elimination of a group of atoms containing three carbon atoms. On the other hand, in the ions with m/e 228 and 230 the methylene group is formed by the decomposition of the spiro center. Consequently, ring D is six-membered and is linked to ring E at the C_{10} atom (IV).

One of the hydroxy groups of ring D is retained in the ion with m/e 258. The position of this hydroxy group at the C_9 atom is excluded by the presence of ions with m/e 228, 230, and 242. The formation of an ion with m/e 258 agrees well with the results of the mass-spectrometric decomposition of α-diols [6]. This is also confirmed by the ion with m/e 270 having a hydroxy group at C_{11}. The formation of this ion takes place with the successive elimination of water and ethylene from the ion $(M-1)^+$. The spectrum also contains the peak of an ion with m/e 298 formed only though the elimination of water. A similar decomposition in the case of bulbocodine [5], which does not contain hydroxy groups in ring D, takes place with the elimination of ethylene. The ion with a mass number of M – 28 has a low intensity in the spectrum of kesselridine.

The definitive structure of kesselridine and the scheme of formation of the ions with m/e 258 and 270 are given above.

A doubly charged ion with m/2e 149 is intensive, which confirms the proposed scheme for the formation of the ion with m/e 298.

The formation of the strongest ions $(M-1)^+$ and $(M-43)^+$ takes place in accordance with the following scheme



The elimination of water from the $(M-43)^+$ ion forms an ion with m/e 256.

EXPERIMENTAL METHOD

The UV spectrum of kesselridine was taken on an SF-4A spectrometer, the IR spectrum on a UR-10 double beam spectrometer, and the NMR spectrum on a Hitachi H-60 spectrometer. The mass spectra were obtained on an MKh-1303 instrument at an energy of the ionizing electrons of 40 eV and a temperature of 100-120°C.

SUMMARY

An investigation of the UV, IR, and NMR spectra of kesselridine has shown that it belongs to compounds of the homoproaporphine type.

A study of the mass-spectrometric fragmentation of kesselridine has permitted the structure of 2,10,11-trihydroxy-1,10-epoxyhexahydrohomoaporphine to be proposed as its most probable structure.

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