We have previously reported the isolation from the epigeal parts of Colchicum kesselringii Rgl. of a new base kesselringine and its partial structure [1, 2]. From the nature of its UV spectrum, this compound differs considerably from the homoproaporphine and proaporphine bases with a dienone ring [3, 4]. Its IR spectrum (Fig. 1) shows the absorption bands of a hydroxy group (3530 cm$^{-1}$), a benzene ring (1600, 900-800 cm$^{-1}$), and methylene groups (1460 cm$^{-1}$).

The NMR spectrum of the alkaloid (Fig. 2) shows three-proton singlets at 2.32 and 3.32 ppm of N-methyl and O-methyl groups, respectively, and a one-proton singlet at 6.42 ppm corresponding to the C$_3$ proton of the benzene ring.

According to its mass spectrum, which has the peaks of the following main ions: m/e 331 (M$^+$, 42%), 330 (M-1)$^+$ (100%), 316, 288 (M-43)$^+$, 256, 244, 242, 238, 230, 228, 165, kesselringine is close to the proaporphine alkaloids of the type of amuramine [5], and probably has the basic skeleton I.

From the spectral characteristics and the elementary composition, it may be concluded that kesselringine is a homoproaporphine compound highly reduced in the dienone ring and is the first representative of substances with a spirocyclohexane ring.

Diazomethane methylates the phenolic hydroxy group of ring A of kesselringine with the formation of O-methylkesselringine (II, Scheme 1).

Judging from the value of its chemical shift (CS) in the PMR spectrum, the methoxy group of kesselringine is located in an alicyclic ring. The base is inert to the action of ammonia and alkalis, but it is readily hydrolyzed by heating in dilute acids, changing into norkesselringine. (III). The hydrolysis of O-methylkesselringine forms O-methylnorkesselringine (IV), which is isomeric with kesselringine. These two compounds differ by the positions of the hydroxy and methoxy groups. The hydrolysis of the alicyclic methoxy group in the formation of O-methylnorkesselringine is shown by the absence of the corresponding CS (three-proton singlet at 3.32 ppm).

![Fig. 1. IR spectrum of kesselringine (in paraffin oil).](image-url)
Fig. 2. NMR spectrum of kesselringine (in CDCl₃).

Scheme 1. Structure and transformations of kesselringine.

from its PMR spectrum and by the appearance of an absorption band of a hydroxy group in the IR spectrum ($\nu_{\text{max}}$ 3650 cm$^{-1}$).

The base underwent no change when it was heated in solution in methanol containing hydrochloric acid. However, in ethanol, n-propanol, and n-butanol a transesterification reaction was observed with the formation of the corresponding alkynorkesselringine (V–VII). In acid aqueous solutions, the latter are hydrolyzed to nor-kesselringine and on methanolyis they are converted into kesselringine.

The transformations of kesselringine reported above shows that its molecule contains a cyclic acetal grouping [6, 7]. Thus, the oxygen bridge and the methoxy group are attached to the same C atom of ring D. Since the formation of the ether bond in the homoproporphine is possible only at the C₁–C₁₂ and C₁–C₁₃ positions [8], the acetal group in ring D can be located at C₁₂ or C₁₃. On studying the structure of the base with Dreiding models, we came to the conclusion that a six-membered ring E, i.e., with acetal group at C₁₂, is the most probable structure for it.

The acetylation of kesselringine with acetic anhydride in the presence of anhydrous sodium acetate led to a O,O,N-triacetyl derivative (VIII). This reaction, taking place with the opening of the nitrogen-containing heterocycle, confirms the presence of a tetrahydroisoquinoline fragment [9] in the molecule of the base. On acetylation with acetic anhydride in the presence of sulfuric acid, however, O,O-diacetylkesselringine (IX) was formed. These reactions show that the base contains, in addition to the phenolic hydroxyl of ring A, another, secondary, alcoholic hydroxy group. By analogy with related proaporphine and homoproaporphine alkaloids, the latter may be assigned to the C₁₁ position. A comparative study of the CSs of a C₁₁ proton in kesselringine and its acetyl derivatives shows that the actual and hydroxy groups in the spirocyclohexane ring are actually located on adjacent carbon atoms: in the PMR spectrum of the initial base the signal of this proton has a CS of 3.72 ppm, and in the products of acetylation, as is well known [10], it shifts downfield and appears at 5.13 ppm in the form of a broadened singlet with a half-width of 5.6 Hz. Consequently, the C₁₂ position of the spirocyclohexane ring is occupied by the acetal group, and the proton at C₁₁ has the equatorial orientation and interacts with only one of the protons of the methylene group at C₁₀.

On the basis of what has been said, kesselringine corresponds to the structure 2,11-dihydroxy-12-methoxyhexahydro-1,12-epoxyhomoproaporphine (I).