THE STRUCTURE OF REGELINONE

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A new alkaloid with the composition $C_{19}H_{19}O_5N$ (M^+ 341) mp 316-317°C, which has been called regelinone (I) has been isolated from the plant *Colchicum kesselringii* Rgl. (*C. regelii* Stef.) [1]. The following characteristics of the base have been found: in the UV spectrum, absorption maxima at 248, 300, and 395 nm (in methanol), and in the IR spectrum absorption bands of a hydroxy group (3240 cm^{-1}), a carbonyl group (1690 cm^{-1}), and the C=C bonds of a benzene ring (1585 cm^{-1}).

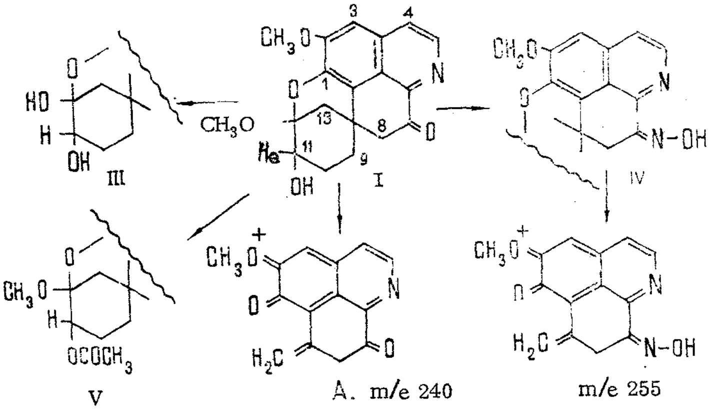
The PMR spectrum of (I) (in CF_3COOH, δ scale) shows the resonance signals of three aromatic protons (2H, s, 7.78 ppm, 1H, s 7.19 ppm), of the protons of two methoxy groups (3H × 2, s, 4.18 and 3.23 ppm), and of one proton geminal to a hydroxy group (1H, 3.88 ppm). When the solution was diluted with deuterated water, the two-proton singlet at 7.78 ppm split into two doublets with chemical shifts of 7.72 and 8.06 ppm and coupling constants of 6.5 Hz, which shows the presence of (I) of a $-CH{=}CH-$ grouping.

The base formed a mono-O-acetyl derivative (II). In the PMR spectrum of (II), the signal of the proton geminal to the acetoxy group had shifted downfield (5.08 ppm). The half-width of the signal of this proton (~ 6.0 Hz) shows its equatorial orientation [2].

The alkaloid had a weakly basic nature. It was stable to the action of dilute alkali but in dilute mineral acids it underwent hydrolysis to a compound (III). This shows the presence of an acetal grouping in it, which is characteristic for the series of homoproaporphine bases of *C. kesselringii* [3, 4]. In addition, the ^{13}C NMR spectrum of (I) had a resonance signal (101.4 ppm confirming the presence in its molecule of carbon connected with an acetal grouping [4]. The quaternary carbon atom of the spiro center of the molecule resonates at 37.0 ppm. On the basis of the facts given, the ^{13}C NMR spectrum, and the biogenetic scheme of Colchicum alkaloids [5], a homoaporphine nitrogen–carbon skeleton was put forward for (I).

The mass spectrum of the base contained the peaks of ions with m/e 341 (M^+, 100%), 326, 298, 242, 241, 240, 228, 227, 213, 212, and others, which are nitrogen-containing fragments. The great difference in the mass spectrum of (I) from known highly reduced homoproaporphine bases [6, 7] can be explained by a considerable difference in the structures of rings B and C.

The facts given and the high-resolution mass spectrum enables the ion with m/e 240.0677 to be assigned structure A (calc. m/e 240.0658).



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A similar ion is observed in the mass spectrum of (II), which shows that the acetoxy (or, in (I), the hydroxy] group is present in ring D. In the mass spectrum of the oxime of the base (IV), an ion with m/e 255 corresponds to this ion (A).

On the basis of the facts given above, structure (I) may be put forward as the most probable for regelinone.

Regelinone is the first representative of the oxohomoproaporphine bases.

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ACETYLBROWNIINE — A NEW ALKALOID FROM *Delphinium oreophilum*

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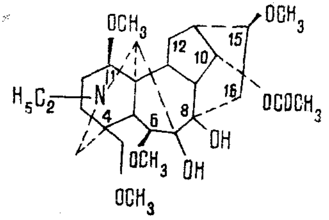
We have investigated the epigeal part of *Delphinium oreophilum* [1, 2] collected in the budding stage in the Dzhungarian Ala-Tau. The total alkaloids amounted to 0.8% of the weight of the air-dry plant. On separating the combined material, we isolated two bases, one of which was obtained in the form of the perchlorate with mp 181-183°C and was identified on the basis of IR spectra, thin-layer chromatography, and a mixed melting point with an authentic sample as methyllycaconitine perchlorate. The second base, with mp 129-130°C, was isolated by separating the mother liquors of the combined alkaloids according to their basicities.

This alkaloid had the composition $C_{27}H_{43}NO_8$ (I). Its IR spectrum contained absorption bands at 3480 and 3430 cm^{-1} (hydroxy groups) and 1743 cm^{-1} (carbonyl of an ester group). The NMR spectrum of the base (JNM-4H-100/100 MHz, $CDCl_3$, internal standard HMDS, δ scale) contained the signals of an ethyl group (three-proton triplet at 0.99 ppm), or an acetoxy group (three-proton singlet at 2.01 ppm) and of four methoxy groups (three-proton singlets at 3.16, 3.21, 3.25, and 3.34 ppm), and a signal with an intensity of one-proton unit at 4.72 ppm (triplet, J = 5 Hz). The position of this signal and the spin—spin coupling constant are characteristic for a proton geminal to an acetoxy group at C_{10} [3, 4].

A direct comparison of the spectral characteristics and the physicochemical constants of (I) with those of browniine monoacetate [5] showed their complete identity.

This is the first time that monoacetylbrowniine has been isolated from a plant.



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