

THE STRUCTURE OF ROEMREFIDINE

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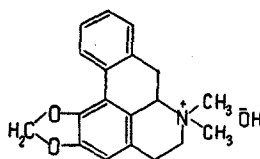
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It has previously been reported that a number of bases have been isolated from the combined alkaloids of Roemeria refracta [1-5].

Continuing the separation of the readily water-soluble fraction of the mixed bases obtained from 470 kg of the plant, we have isolated 140 mg of crystals with mp 223-224° C (from aqueous methanol).

From its properties the base is a new one, and we have called it roemrefidine. The UV spectrum has maxima in the 270 and 315 mμ regions (log ε 4.26 and 3.73, respectively). The spectra of roemrefidine is similar to that of michepressine iodide [6]. Roemrefidine does not contain methoxy, hydroxy, or carbonyl groups and gives positive reactions for a methylenedioxy group with chromotropic, gallic, and phloroglucinol sulfuric acids. A comparison of the IR and UV spectra of this substance and of 7-isoroemerine methiodide [2,3] have shown that they are completely identical. A mixture with 7-isoroemerine methiodide likewise gave no depression of the melting point.

Roemrefidine has been isolated in the form of the iodide and is the quaternary form of the 7-isoroemerine



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ALKALOIDS OF THE ROOTS OF THALICTRUM FLAVUM

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The roots of Th. flavum L. collected in the period of vigorous growth of the plant, 20-25 May 1962 in the Chon-Kemin valley, Kirgiz SSR, were extracted with chloroform, and 1.55% of total alkaloids was isolated. From the chloroform fraction of the mixture of bases, 0.3% of berberine has been obtained in the form of the chloride [1].

The ethereal fraction of the total alkaloids was treated with methanol. Greenish needle-like crystals of an optically inactive phenolic base with mp 133-135° C (decomp) were formed. Its IR spectrum: λ_{max} 236, 264, 314, 338 mμ (log ε 4.36, 4.56, 4.12, 3.72).

The IR spectrum of the base has absorption bands at 1722 cm⁻¹ (carbonyl), 3400 (hydroxyl), 1277, 1230 (methoxyl), and 1040 cm⁻¹ (methylenedioxy group). The properties of this base are very similar to those of thalicsine [2] and it is apparently new.

The mother liquors were separated into phenolic and nonphenolic fractions. The mixture of nonphenolic bases

was separated according to their basicities into 10 fractions, and from the 10-th fraction we obtained thalisopyrine, isolated previously from *Th. isopyroides* [3]. From a comparison of the UV and IR spectra, paper chromatography, and the melting point of a mixture, thalisopyrine was identical with an authentic sample of cryptopine kindly provided by Dr. J. Slavik (Czechoslovakia).

After chloroform extraction, the raw material was dried and covered with methanol. Six decantations were performed. The methanolic extract was evaporated and the residue was dissolved in 5% hydrochloric acid. The acid solution was washed with chloroform, and 0.03% of berberine chloride was isolated from it. Potassium iodide was added to the solution and the white crystals that deposited were separated off and identified as magnoflorine iodide. Yield 1.04%.

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NMR SPECTRUM OF FOLIOSIDINE

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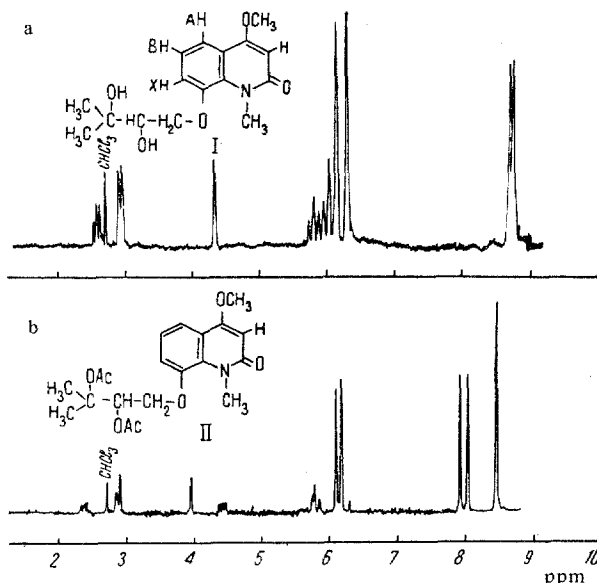
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We have studied the NMR spectrum of foliosidine (I) [1] and O,O-diacetylfoliosidine (II) obtained on a JNM-4H-100/100 MHz instrument (internal standard HMDS, the signal of which was taken as 10 on the τ scale).

In the NMR spectrum of (I) (figure, a) the signals of three aromatic protons forming an ABX system appear clearly, but because of the closeness of the chemical shifts (CS) many peaks coincide. Consequently the proton X forms a distorted quartet with a center at $\tau = 2.60$ ppm; the two-proton doublet at 2.97 ppm, $J = 6.0$ Hz, relates to the AB protons. The one-proton singlet at 4.35 ppm corresponds to a β proton.

The molecule of (I) contains four CH_3 groups giving rise to four singlets in the NMR spectrum: $\text{OCH}_3 - 6.15$, $\text{N}-\text{CH}_3 - 6.30$ ppm and two CH_3 groups on quaternary carbon atoms—a doublet at 8.68 and 8.76 ppm which shows their nonequivalence, evidently because of the influence on them of the oxygen atom of the OH group. This is also shown by the CS of the protons mentioned, which are shifted slightly to the weak-field region. The total intensity of the signals of the multiplet at 5.90 ppm in (I) (see figure, a) is five proton units. Consequently, in this region the signals of the protons of a CH_2-O group, two OH groups, and a methine proton coincide. The latter assumption is justified by the fact that in the spectrum of (II) (figure, b) in this region the signals of the two OH groups are completely absent and the signal of the HCOH proton undergoes a paramagnetic shift on acetylation and appears at 4.45 ppm, i.e., in the 5.80 ppm region. The signal of the remaining two-proton quartet corresponds to CH_2-O .

The nature of the splitting of the HCOAc proton at 4.45 ppm—a quartet with $J_1 = 7.5$ Hz and $J_2 = 3.0$ Hz—shows the nonequivalence of the CH_2 protons. The signals at 7.94 and 8.06 ppm relate to 2 OCOCH_3 and to the two CH_3 groups, since on acetylation a deshielding action of the $\text{C}=\text{O}$ group and a shift of the signal of the two CH_3 groups into the weak field by $\Delta\tau = 0.32$ ppm is found. The position of the signals of the β proton of the ring B and the X proton show that the side chain of (I) and (II) is located above or below the plane of the ring: on acetylation the β



NMR spectra of foliosidine (a) and O,O-diacetylfoliosidine (b) in CDCl_3 .