LEPTORHABINE – A NEW ALKALOID FROM Leptorhabdos parviflora

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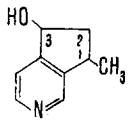
We have investigated the epigeal part of the plant L. parviflora collected in the valley of the R. Talas (close to the town of Dzhambul) in the flowering period. When the combined ether-soluble alkaloids were separated on a column of alumina, from ether–chloroform (10:2) eluates we isolated a liquid base with the composition $C_9H_{11}NO$, $[\alpha]_D^{20}+10°$ (c 1.015; chloroform); M^+ 149; R_f 0.56 [TLC on silica gel in the benzene–methanol (4:1) system]. The UV spectrum of the base has two maxima at λ_{max} 263, 269 nm (log ε 3.36, 3.33) which are characteristic for alkaloids of the pyridine type [1-4]. In the IR spectrum of the base, absorption bands appear at 3400-3200 cm^{-1} (OH), 2980-2940 cm^{-1} (C–CH_3), and 1605 and 1580 cm^{-1} (pyridine ring). The base is a new one and we have called it leptorhabine.

In the NMR spectrum of leptorhabine (JNM-4H-100/100 MHz in CCl_4, internal standard HMDS, δ scale) a one-proton singlet can be clearly seen at 8.11 ppm and also two one-proton doublets at 8.07 and 7.15 ppm (J = 5.0 Hz) corresponding to three aromatic hydrogen atoms in the α-, α'-, and β'-positions with respect to the nitrogen atom of the pyridine ring. The absence of other signals in this region and the production of pyridine-3,4-dicarboxylic acid by the oxidation of the base with $KMnO_4$ in an alkaline medium shows the positions of the substituent in the pyridine ring.

The one-proton signal at 6.94 ppm from the proton of the hydroxy group is shifted downfield, which is explained by the presence of a hydroxy group on a carbon atom directly conjugated with an aromatic nucleus. A three-proton doublet at 1.20 ppm (J = 7.0 Hz) is due to the protons of a methyl group, and a two-proton multiplet at 1.97 ppm to two methylene protons. Two one-proton multiplets at 5.06 and 3.30 ppm relate to the two methine protons at C_1 and C_3.

In the NMR spectrum of O-acetylleptorhabine the signal of the proton of the hydroxy group has disappeared and a three-proton singlet has appeared at 1.92 ppm from the CH_3–C =O group, and the signal of one methine proton has shifted from 5.06 ppm to 5.99 ppm.



The mass spectrum of leptorhabine shows peaks of ions with m/e 149 (M^+), 132, 131, 118, 117, 106, 104, 79, 77, 65, 63. What has been said above has enabled us to suggest for leptorhabine two possible structures: 1-hydroxy-3-methylcyclopenta[d]pyridine and 1-methyl-3-hydroxycyclopenta[d]pyridine. From a comparison of the NMR spectrum of leptorhabine with literature data [3, 4], a consideration of Dreiding models [descreening influence of the acetyl group on the α- and α'-protons (δ 8.34; 8.25 ppm) and the absence of such screening for the β'-proton (7.17 ppm)] and also from biogenetic considerations, we consider the above structure to be most probable.

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