STRUCTURE OF BADRAKEMIN

V. Yu. Bagirov, N. P. Kir'yalov, V. I. Sheichenko, and V. N. Bochkarov

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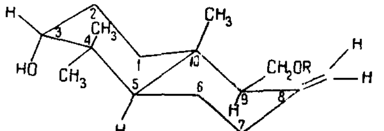
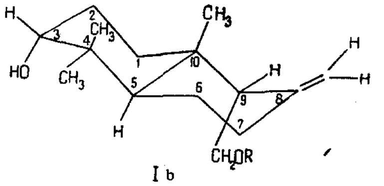
The results of a comparison of the mass spectra of badrakemin [1] and gummosin [2] taken under similar conditions (MKh-1303 instrument, introduction into the source, E 50, t 160° C) did not show the presence of any peaks differing in their m/e values. However, while in the mass spectrum of badrakemin the relative intensities of the peaks with m/e 382 (M^+), 221 $(M - RO)^+$, 220 $(M - ROH)^+$, 203 $(M - RO - H_2O)^+$, and 162 $(ROH)^+$ (where R represents the umbelliferone residue) amount to 55,5, 16, 70, and 100%, respectively, the intensities of the same peaks in the mass spectrum of gummosin are 32, 4, 5, 100, and 67%. Close similarity of the mass spectra (with some differences in the intensities of the individual peaks) is chracteristic for stereoisomers [3]. The NMR spectra of gummosin and badrakemin in $CDCl_3$ solution (JNM-4H-100) differ substantially in the positions of the signals of some protons. Thus, for example, while in gummosin the methylene protons of the $> CH-CH_2-O-R$ fragment are represented by two signals with centers at 4.43 ppm* ($|J_{gem}| = 10$ Hz, $J_{vic} = 5$ Hz) and 4.11 ppm ($|J_{gem}| = 10$ Hz, $J_{vic} = 7$ Hz), in badrakemin the same protons are represented by a single signal with a center at 4.21 ppm. In gummosin the signals of the protons of the exocyclic methylene group appear at 4.72 and 4.82 ppm, and in badrakemin the protons of the same group give signals at 4.55 and 4.93 ppm. The positions of the signals of the protons of the methyl group at C_{10} in badrakemin and gummosin are also different (0.87 and 1.02 ppm, respectively). The signals of the protons of the gem-dimethyl group in these compounds occupy similar positions (1.01 and 0.87 ppm, and 1.02 and 0.87 ppm, respectively). The difference in the positions of the signals of the protons of the methyl groups at C_{10} is retained in gummosin (1.22 ppm) and badrakemin (1.09 ppm), while the positions of the signals of the protons of the methyl groups at C_4 in these compounds coincide (1.07 and 1.16 ppm). The considerable upfield shift of the signal of one of the protons of the exocyclic methylene group in badrakemin compared with gummosin can be explained by the closer spatial propinquity of the substituent at C_9 to this proton in badrakemin. The upfield displacement of the signals of the protons of the angular methyl group on passing from gummosin to badrakemin is also apparently due to the screening action of the $>C_9H-CH_2-O-R$ fragment. Consequently, in badrakemin the substituent at C_9 probably occupies the equatorial position and in gummosin the axial position, i. e., the substituent at C_9 and the angular methyl group are in the cis position in badrakemin (Ia) and in the trans position in gummosin (Ib) (see also [4]).



I a



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*The chemical shifts are given relative to the signal of TMS (0δ ppm).

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Komarov Institute of Botany, AS AzerbSSR
Komarov Botanical Institute, AS USSR
Institute of the Chemistry of Natural Compounds, AS USSR