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# Synthesis and Study of Tautomerism of 7(8)-Hydroxypyranonaphthazarins by IR-Spectroscopy

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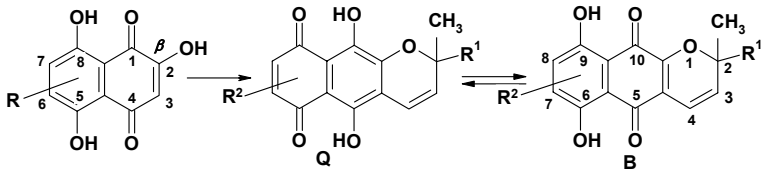
Recently, we have stated a convenient and accurate method based on IR spectral parameters of β-OH groups to measure the quantitative composition of tautomeric equilibrium in monohydroxynaphthazarin derivatives.[1] Now we used this approach for the determination of the tautomeric ratio of 7(8)-hydroxypyranonaphthazarins in solutions. For this purpose the compounds **1** and **2** were prepared by the reaction of correspondent naphthoquinones **3** and **4** with citral (Scheme 1). Hydroxypyranonaphthazarin **5**, a pigment isolated from the sea urchins *Echinothrix diadema* and *E. calamaris*[2] was synthesized by the reaction of mompain (**3**) with crotonic aldehyde.




**3.** R=7-OH
**4.** R=6-OH

**1.** $R^1$=-$(CH_2)_2CHC(CH_3)_2$, $R^2$=8-OH
**2.** $R^1$=-$(CH_2)_2CHC(CH_3)_2$,$R^2$=7-OH
**5.** $R^1$=H, $R^2$=8-OH

**Scheme 1**

It has been shown that hydroxypyranonaphthazarins **1, 2, 5** exist in organic aprotic solvents as mixtures of tautomeric forms **Q** and **B** (Scheme 1). The stretching vibration frequencies of β-OH groups in the IR spectra of compounds **1, 2, 5** are in good agreement with the ranges of the corresponding values found for 2-hydroxy-6,(7)-methoxynaphthazarins.[1] This allows to estimate the percentage of each tautomer in aprotic media. It has been established that the compounds **1** and **2** in $CCl_4$ exist as forms **B** and **Q** in the ratio 22 : 78 and 18 : 82, respectively. So the position of β-OH group relatively to the oxygen atom of the pyrano ring of these compounds has not significantly influence on the tautomeric composition. For the solution of pigment **5** in $CCl_4$ this proportion is 19 : 81.

**References**:

**1**. V.P. Glazunov, A.Ya. Tchizhova, N.D. Pokhilo, V.Ph. Anufriev, G.B. Elyakov, *Tetrahedron*, **2002**, *58*, 1751;

**2**. R.E. Moore, H. Singh, P.J. Scheuer, *Tetrahedron Lett*., **1968**, *43*, 4581.