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# NOVEL METHOD FOR SYNTHESIS OF 2,3,6,7,12,13,16,17-OCTAHYDRO-1H,5H,11H,15H-DIQUINOLIZINO-[1,9-*bc*:1',9'-*hi*]XANTHYLIUM PERCHLORATE

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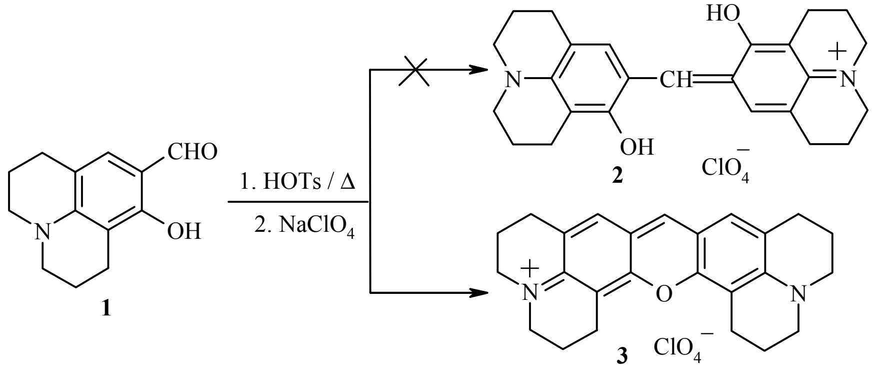
**Keywords:** 8-hydroxyjulolidine, pyronine, polymethine dyes, fluorescence.

Goal-directed search for long-wavelength fluorescent dyes is an important problem in the chemistry of polymethines [1]. One of the principal methods for solving this problem is to search for new heterocyclic rings or to modify known heterocyclic rings in order to construct polymethine dyes.

We know that polymethine dyes, derivatives of julolidine (2,3,5,7,6,9-hexahydrobenzo[*i,j*]quinolizine), are characterized by rather intense long-wavelength absorption bands [2].

With the aim of obtaining new polymethine dyes that are analogs of julolidine dyes (8-hydroxyjulolidine derivatives), we have studied the reaction of self-condensation of 9-formyl-8-hydroxyjulolidine **1**, which was carried out according to the procedure in [3]. We found that when compound **1** was fused with excess *p*-toluenesulfonic acid, the pyronine **3** was formed rather than the expected dye **2** [2].



Reference to compound **3**, as the intermediate product in synthesis of some laser dyes of the rhodamine class obtained by a more complicated method and in lower yield, is encountered only in patent [4].

The proposed synthesis method allows us to obtain the intensely fluorescing compound **3** (ϕ = 95%) in good yield, which makes it promising for further use.

Thus 8-hydroxyjulolidine-9-carbaldehyde **1** (1.1 g, 5.1 mmol) and *p*-toluenesulfonic acid monohydrate (0.9 g, 4.7 mmol) were fused for 30-40 min at 120-130°C. After cooling, the reaction mass was dissolved in 30 ml acetic acid, and to the hot solution was added a solution of sodium perchlorate monohydrate (1 g) in

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acetic acid (10 ml). The precipitate was filtered out and washed with ether. Yield 0.35 g (42%); mp 264-266°C (decomposition). UV spectrum: $\lambda_{max}$ (Shimadzu UV-3100, $CH_3CN$) 574 nm, $\varepsilon \cdot 10^{-3}$ 110.6; $\lambda_{em}$ (Cary Eclipse, $CH_3CN$) 599 nm (excitation at 530 nm). $^1H$ NMR spectrum (Varian VXR-300, 300 MHz, DMSO-$d_6$, TMS), $\delta$, ppm: 1.95 (8H, m, $N–CH_2CH_2\underline{CH_2}$); 2.81 (4H, m, $N–CH_2\underline{CH_2}CH_2$); 2.9 (4H, m, $N–CH_2\underline{CH_2}CH_2$); 3.51 (8H, m, $N–CH_2CH_2\underline{CH_2}$); 7.4 (2H, s, 8-H, 10-H); 8.33 (1H, s, 9-H). Found, %: C 64.0; H 5.9; Cl 7.5; N 5.8. $C_{25}H_{27}ClN_2O_5$. Calculated, %: C 63.8; H 5.9; Cl 7.6; N 5.9.

## REFERENCES

1. J. Fabian, H. Nakazumi, and M. Matsuoka, *Chem. Rev.*, **92**, 1197 (1992).
2. F. A. Mikhailenko and L. V. Balina, *Khim. Geterotsikl. Soedin.*, 450 (1982).
3. F. A. Mikhailenko and L. I. Shevchuk, *Synthesis*, **10**, 621 (1973).
4. K. Drexhage, H. Harnish, and R. Raue, Ger. Patent 3322945; *Chem. Abstr.* **102**:115142 (1985).