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NOVEL COUMARIN HYDROZONES

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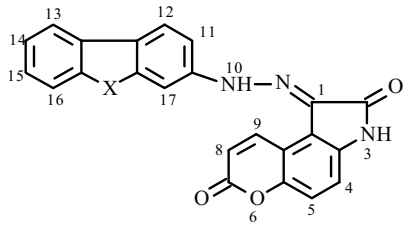
Coumarins are a structurally diverse class of natural plant bioregulators. Depending on the structure, coumarins and their analogs exhibit different types of biological activity [1]. The high biological activity of coumarins is associated with the presence of a lactone ring, a double bond in the 3,4-position, etc. Derivatives of dibenzofuran and dibenzothiophene also exhibit high pharmacological activity [2].

We synthesized structures in which a coumarin derivative and dibenzothiophene or dibenzofuran were joined into a single molecule in order to study the mutual influence of these two structures on the biological activity. This resulted in the preparation of the novel heterocyclic systems 2,6,7-trioxo-1,2-dihydro-7α-pyrano[3,2-*e*]indol-1-(dibenzothiophen-3-yl)hydrazone (**1**) and 2,6,7-trioxo-1,2-dihydro-7α-pyrano[3,2-*e*]indol-1-(dibenzofuran-3-yl)hydrazone (**2**).



1, 2

X = S (**1**), O (**2**)

The dioxodihydropyrrolocoumarin was synthesized by the literature method [3] starting with the reaction of 6-aminocoumarin with a mixture of chloral hydrate and hydroxylamine in acidic medium. Cyclization of the resulting 6-isonitrosoacetamidocoumarin isolated 1,2-dioxo-1,2-dihydropyrano[3,2-*e*]indole, reaction of which with a hot EtOH solution of dibenzothiophene hydrazine in acidic medium produced **1**. Crystallization from EtOH afforded pure **1**, mp 327–330°C. IR spectrum (KBr, ν, cm^{-1}): 3415 (NH), 3255 (NH…O=C), 1720 (C=O). The starting dibenzothiophene hydrazine was prepared from 3-aminodibenzothiophene by the usual method [4].

Heterocycle **2** was prepared analogously to **1** from dibenzofuran hydrazine and dioxodihydropyrrolocoumarin, mp 341–343°C. IR spectrum (KBr, ν, cm^{-1}): 3410 (NH), 3255 (NH…O=C), 1735 (C=O).

The structures of **1** and **2** were confirmed by IR and PMR spectral data.

2,6,7-Trioxo-1,2-dihydro-7α-pyrano[3,2-*e*]indol-1-(dibenzothiophen-3-yl)hydrazone (1). PMR spectrum (DMSO-d_6, δ, ppm, J/Hz): 11.2 (1H, br.s, H-3), 7.12 (1H, d, J = 8.8, H-4), 7.21 (1H, d, J = 8.8, H-5), 8.72 (1H, d, J = 9.3, H-8), 6.66 (1H, d, J = 9.3, H-9), 13.36 (1H, s, H-10), 7.71 (1H, dd, J = 8.3, 1.5, H-11), 8.00 (1H, d, J = 8.3, H-12), 7.99 (1H, d, J = 8.2, H-13), 7.5 (2H, m, H-14, 15), 8.39 (1H, d, J = 8.3, H-16), 8.31 (1H, d, J = 1.5, H-17).

2,6,7-Trioxo-1,2-dihydro-7α-pyrano[3,2-*e*]indol-1-(dibenzofuran-3-yl)hydrazone (2). PMR spectrum (DMSO-d_6, δ, ppm, J/Hz): 11.1 (1H, br.s, H-3), 7.15 (1H, d, J = 8.8, H-4), 7.2 (1H, d, J = 8.8, H-5), 8.75 (1H, d, J = 9.3, H-8), 6.67 (1H, d, J = 9.3, H-9), 13.3 (1H, s, H-10), 7.49 (1H, dd, J = 8.3, 1.5, H-11), 8.09 (1H, d, J = 8.3, H-12), 8.07 (1H, d, J = 8.3, H-13), 7.4 (2H, m, H-14, 15), 7.65 (1H, d, J = 8.3, H-16), 7.83 (1H, d, J = 1.5, H-17).

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