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1-THIOCARBAMOYL-5-OXY- AND 5-THIOSEMICARBAZIDO-2-PYRAZOLINES

K. N. Zelenin, A. B. Tomchin,
O. V. Solod, and M. Yu. Malov

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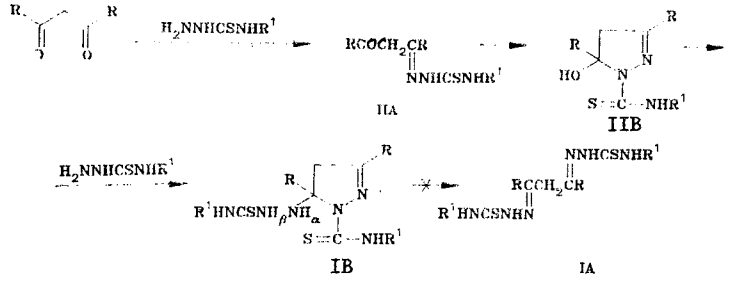
Products of the condensation of 1,3-diketones with thiosemicarbazide and its N^3-substituted homologs in a 1:2 ratio have an antitumorigenic activity. These compounds I were assumed to be bisthiosemicarbazones A [1-3], but their structure has not yet been studied.

We found that compounds I have actually a cyclic pyrazoline structure B, and not the linear structure A. We shall add that also the condensation products of these reagents in a ratio of 1:1 (II) are not monohydrazones A, as assumed in [3, 4], but the corresponding 5-hydroxypyrazolines B.



Ia-c, IIa R = CH_3, IIb R = C_6H_5; Ia, IIb R^1 = H, Ib, IIa R^1 = CH_3, Ic R^1 = C_2H_5.

Compound Ia [3]. PMR spectrum (Py-D_5): 1.58 (3H, t, J = 0.6 Hz, 3-CH_3), 1.75 (3H, s, 5-CH_3), 2.53 and 3.15 (AB system, J_{AB}^1 = 18 Hz, J^2 = 0.6 Hz, 2H, CH_2), 7.30 (1H, s, NHα), 7.96, 8.20 (2H, s, $CSNH_2$), 8.90, 9.17 (2H, s, $CSNH_2$), 9.45 ppm (1H, s, NHβ).

Derivative Ib [3]. PMR spectrum ($CDCl_3$): 1.72 (3H, s, 5-CH_3), 1.91 (3H, t, J = 0.6 Hz, 3-CH_3), 2.58 and 2.92 (AB system, J_{AB}^1 = 18 Hz, J^2 = 0.6 Hz, 2H, CH_2), 3.01 (3H, d, 5Hz, N–CH_3), 3.09 (3H, d, 5 Hz, N–CH_3), 6.65, 6.91 (2H, s, 2NH), 7.35 ppm (2H, m, 2NHCH_3).

Compound Ic [3]. PMR spectrum ($CDCl_3$): 1.15 (6H, t, J = 7 Hz, 2C_2H_5), 1.73 (3H, s, 5-CH_3), 1.93 (3H, t, J = 0.8 Hz, 3-CH_3), 2.61 and 2.91 (AB system, J_{AB}^1 = 18 Hz, J^2 = 0.8 Hz, 2H, CH_2), 3.3-3.8 (4H, m, 2C_2H_5), 6.61, 6.85 (2H, s, 2NH), 7.3 ppm (2H, m 2NHC_2H_5). ^{13}C NMR spectrum (DMSO-D_6): 14.5 and 14.6 (q, CH_3CH_2N), 15.9 (q, 3-CH_3), 23.5 (q, 5-CH_3), 37.7 (t, CH_3CH_2N), 47.1 (t, 4-C), 84.6 (s, 5-C), 154.4 (s, C=N), 174.0 and 181.8 ppm (s, 2C=S).

Derivative IIa was obtained by condensation of acetylacetone with N^3-methylthiosemicarbazide in aqueous acetic acid. Mp 95-97°C. PMR spectrum ($CDCl_3$): 1.87 (3H, s, 5-CH_3), 1.94 (3H, t, J_{H-CH} = 1 Hz, 2-CH_3), 2.79 and 3.07 (AB system, J_{AB}^1 = 18 Hz, J^2 = 1 Hz, 2H, CH_2), 3.00 (3H, d, J = 4 Hz, NCH_3), 6.30 (1H, s, OH), 7.25 (1H, m, NH). Found: C 44.7; H 7.2; N 22.3%. $C_7H_{13}N_3OS$. Calculated: C 44.9; H 7.0; N 22.4%.

Compound IIb [4]. PMR spectrum (DMSO-D_6): 4.16 and 3.84 (AB system, J = 19 Hz, 2H, CH_2), 6.80 (1H, s, OH), 7.5-8.2 (10H, m H_{arom}), 8.45, 8.65 ppm (2H, s, NH_2). ^{13}C NMR spectrum (DMSO-D_6): 51.4 (4-CH_2), 95.4 (5-C, 151.8 (C=N), 175.4 (C=S), 124.0-145.1 ppm (C_{arom}, 8 signals).

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Our data agree with those known on the structure of malonodialdehyde bisthiosemicarbazone [5]. The pyrazoline structure of the above described compounds is interesting in connection with the search for antitumorigenic preparations, which in their activity are not inferior to bisthiosemicarbazones of 1,2- and 1,4-dioxo compounds [1].

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