2,3,4,6,7,8-Hexahydro-7-(2-difluoromethoxyphenyl)-6,8-dioxofuro[3,4-b]pyrrolo[3,4-e]pyridine (II). A solution of 1.75 g (0.04 mole) of tetrahydrofuro[3,4-b]pyridine I in 20 ml of ethanol and 6.25 ml (0.05 mole) of a 30% aqueous solution of methylamine was stirred for 4 h, after which 50 ml of water was added, and the precipitate was crystallized from acetone to give 0.3 g (22%) of colorless crystals of II with mp 269-271°C. UV spectrum, λ_{max} (log ε): 212 (4.22), 331 nm (3.88). IR spectrum: 1657, 1686, 1760, 3120, 3182 cm^{-1}. PMR spectrum ($CDCl_3$): δ 2.69 (3H, s, $N-CH_3$), 3.98 (2H, s, CH_2N), 4.81 (3H, s, CH_2O and 4-H), 7.14 (1H, t, J = 75 Hz, CHF_2), 6.9-7.3 ppm (5H, m, Ar—H and NH). Mass spectrum, m/z: 348 $[M]^+$, 320 $[M - CO]^+$, 284, 279 $[320 - CH_3CN]^+$, 272, 268, 251 $[279 - CO]^+$, 208 $[M - C_6H_4OCHF_2 + 3H]^+$, 205 $[M - C_6H_4OCHF_2]^+$, 176 $[205 - CHO]^+$.

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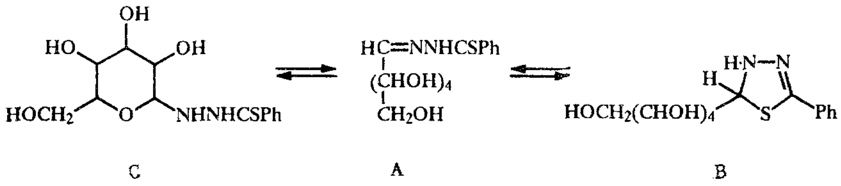
THIOBENZOYLHYDRAZINOPYRANOSIDE—1,3,4-THIADIAZOLINE RING-CHAIN EQUILIBRIUM FOR GLUCOSE THIOBENZOYLHYDRAZONE

V. V. Alekseev and K. N. Zelenin

Arabinose thiobenzoylhydrazone [1], the structure of which has not been studied, is the only known monose (monosaccharide) thiobenzoylhydrazone. If one takes into account the tendency of aldehyde thiobenzoylhydrazones to exist in the 1,3,4-thiadiazoline form [2] and the tendency of aldose hydrazones to exist in the pyranose form [3-5], a ring-chain equilibrium between them is likely for such substances.

It was found that thiobenzoylhydrazone I, which we synthesized in 80% yield (by refluxing thiobenzhydrazide with mannose in methanol) exists in solution in d_6-DMSO in the form of a tautomeric mixture of linear form A (signals of a C=S carbon atom at 183.0 ppm and of a C=N carbon atom at 144.8 ppm) and a cyclic tautomer, which can, with confidence, be identified as 1,3,4-thiadiazoline derivative B, since its spectrum contains signals at 143.0 and 77.6 ppm of the $C_{(2)}$ and $C_{(5)}$ atoms of this ring [2].



I glucose II mannose

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Yet another cyclic tautomer C, to which signals of a C=S carbon atom at 185.0 ppm and $C_{(1)}$ and $C_{(5)}$ atoms of the β-pyranose form at 89.7 and 78.4 ppm correspond [3, 5], is present in addition to these forms in the equilibrium mixture of glucose thiobenzoylhydrazone II.

Compound I. This compound had mp 194-195°C (from methanol). ^{13}C NMR spectrum: form A (20%): 183.0 (C=S), 144.8 (C=N), 132.0 (C_i), 74.3, 73.7, 71.5, 70.2, 64.0; form B (80%): 143.0 [$C_{(2)}$], 131.9 (C_i), 77.6 [$C_{(5)}$], 71.5, 71.2, 70.8, 69.9, 64.0 ppm.

Compound II. This compound had mp 188-189°C (from methanol). ^{13}C NMR spectrum: form A (45%): 184.2 (C=S), 144.3 (C=N), 131.8 (C_i), 74.8, 72.9, 71.7, 69.6, 63.5; form B (45%): 143.0 [$C_{(2)}$], 131.6 (C_i), 76.0 [$C_{(5)}$], 75.2, 73.5, 71.8, 68.5, 63.4; form C (10%): 185.0 (C=S), 130.8 (C_i), 89.7 [$C_{(1)}$], 78.4 [$C_{(5)}$], 77.3, 71.9, 70.7, 61.9 ppm.

The signals of the o-, m-, and p-carbon atoms of the benzene ring of I and II are similar for the various forms and are found at 126.1-129.4 ppm.

Since the tautomeric equilibrium in solutions of I and II is established instantaneously, it is not possible to form a judgment regarding the structures of these compounds in the crystalline state from the NMR data. Satisfactory results of elementary analysis for C, H, and N were obtained for these compounds, and the purity was monitored by TLC on Silufol with butanol—water—acetone (8:1:1) as the eluent.

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