ACETYLATION OF ESTERS OF DL-DIHYDROOROTIC ACID

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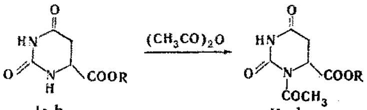
Continuing a study of 4,5-dihydro derivatives of 2,6-dihydroxypyrimidines, we have carried out the acetylation of the methyl and n-butyl esters of DL-dihydroorotic acid (Ia, b) with acetic anhydride.



Ia,b IIa,b

I, II a R = CH_3; b R = C_4H_9

This gives the mono-N^3-acetylated esters of DL-dihydroorotic acid (IIa, b), the structure of which is confirmed by the bathochromic shift in the UV spectrum in an alkaline medium [1]. The formation of the mono-N^3-acetylated derivatives in the reaction with acetic anhydride is characteristic for derivatives of 2,6-dihydroxypyrimidine [2] and has been shown for 4,5-dihydrouracil [3].

n-Butyl DL-N^3-acetyl-4,5-dihydroorate (IIb). A mixture of 1 g of Ib and 10 ml of $(CH_3CO)_2O$ was boiled for 2 hr. After dilution with water, the yellow oily IIb (not contaminated with Ib) precipitated, with R_f 0.96 (ascending chromatography on FN-1 paper in system "A": n-$C_4H_9OH-CH_3COOH-H_2O$ (4:1:1)). The IIb was treated with water several times and was evaporated in vacuum. Then it was heated in methanol with the addition of active carbon. The filtrate was evaporated to dryness and the residue was recrystallized from a large volume of water, being kept in the refrigerator until the precipitate deposited (several days). The precipitate was dried over P_2O_5. The yield of IIb was 0.38 g (34%), mp 57°C. IR spectrum (IKS-14 instrument, Nujol), cm^{-1}: 3268 (NH), 1755 (ester CO), 1738, 1706 (CO of cyclic and acylic amides). UV spectrum (UV-2 automatic spectrophotometer): λ_{max} (pH 7) 212 nm (ε = 10,600); λ_{max} (0.1 N NaOH) 238 nm (before decomposition). Found %: C 51.51; H 6.09; N 11.03. $C_{11}H_{16}N_2O_4$. Calculated %: C 51.54; H 6.20; N10.92.

Methyl DL-N^3-acetyl-4,5-dihydroorotate (IIa). This was obtained similarly. The yield after purification was 31%, mp 108-109°C (from water), R_f 0.88 (system "a"), UV spectrum: λ_{max} (pH 7), 212 nm (ε = 11,800), λ_{max} (0.1 N NaOH), 238 nm (before decomposition). Found %: C 45.11; H 4.72; N 12.91. $C_8H_{10}N_2O_5$. Calculated %: C 44.86; H 4.70; N13.08.

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