NEW PYRIMIDYL-N-α-AMINO ACIDS

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Only one representative of the α-amino-β-(N_1-uracilyl) propionic acids has been known hitherto, β-(N_1-uracilyl)-α-alanine (willardine) (I), which was first isolated from a number of plant materials [1, 2]. The synthesis of willardine and the resolution of its racemate have recently been reported [3–5]. We have obtained for the first time, by the above-mentioned procedure [3, 4] the following analogs of willardine, α-amino-β-(5-methyl-N_1-uracilyl)- (II), α-amino-β-(5-fluoro-N_1-uracilyl)- (III), and α-amino-β-(4-cytosin-N_1-yl)propionic acid (IV). The reaction of I with elementary bromine and with N-chlorosuccinimide has given α-amino-β-(5-bromo-N_1-uracilyl)- (V) and α-amino-β-(5-chloro-N_1-uracilyl)propionic (VI) acids, respectively. The investigation of the physiological activity of the substance is proceeding.

α-Amino-β-(5-methyl-N_1-uracilyl)propionic acid (II), mp 218° C (decomp, from water). Found, %: C 42.07; H 5.35; N 18.74. Calculated for $C_8H_{11}N_3O_4 \cdot H_2O$, %: C 41.55; H 5.69; N 18.17%. R_f 0.22 (system 1); 0.80 (system 2); 0.45 (system 3).[*] UV spectra: λ_{max} 262 nm (log ε 3.7853) (0.1 N HCl); λ_{max} 265 (log ε 3.6415) (0.1 N NaOH).

α-Amino-β-(5-fluoro-N_1-uracilyl)propionic acid (III), mp 213–215° C (decomp, from water). Found, %: C 35.97; H 4.07; N 18.45; F 8.06. Calculated for $C_7H_8FN_3O_4 \cdot H_2O$, %: C 35.75 H 4.21; N 17.87; F 8.06. R_f 0.20 (system 1); 0.81 (system 2); 0.23 (system 3). UV spectrum: λ_{max} 267 nm (log ε 3.5378) (0.1 N HCl); λ_{max} 270 nm (log ε 3.5092) (0.1 N NaOH).

α-Amino-β-(4-cytosin-N_1-yl)propionic acid (IV), mp 216–217° C (from water). Found, %: C 38.89; H 5.84; N 25.48. Calculated for $C_7H_{10}N_4O_3 \cdot H_2O$, %: C 38.88; H 5.59; N 25.91. R_f 0.59 (system 1); 0.55 (system 3). UV spectra: λ_{max} 277 nm (log ε 3.4753) (0.1 N HCl); λ_{max} 274 nm (log ε 3.2679) (0.1 N NaOH).

α-Amino-β-(5-bromo-N_1-uracilyl)propionic acid (IV), mp 210.5–211.5° C (decomp, from water). Found, %: C 28.29; H 3.61; N 13.99; Br 26.71. Calculated for $C_7H_8BrN_3O_4 \cdot H_2O$, %: C 28.39; H 3.41; N 14.18; Br 26.98. R_f 0.13 (system 1); 0.76 (system 2); 0.30 (system 3). UV spectra: λ_{max} 277 nm (log ε 3.7332) (0.1 N HCl); λ_{max} 275 nm (log ε 3.5832) (0.1 N NaOH).

α-Amino-β-(5-chloro-N_1-uracilyl)propionic acid (V), mp 220–221° C (decomp, from water). Found, %: C 36.10; H 3.69; Cl 15.18; N 18.59. Calculated for $C_7H_8ClN_3O_4$, %: C 35.98; H 3.45; Cl 15.21; N 17.98. R_f 0.15 (system 1); 0.82 (system 2); 0.28 (system 3). UV spectra: λ_{max} 277 nm (log ε 3.7332) (0.1 N HCl); λ_{max} 275 nm (log ε 3.5832) (0.1 N NaOH).

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[*] System 1: n-C_4H_9OH – CH_3CO_2H – H_2O (4:1:5); system 2: iso-$C_5H_{11}OH$ – 5% Na_2HPO_4 (1:1); system 3: iso-C_3H_7OH – NH_4OH – H_2O (7:1:2).

SYNTHESIS OF 4-OXO-1,2,4-TRIAZINO[4,5-*a*] BENZIMIDAZOLE AND SOME OF ITS DERIVATIVES

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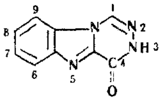
We have effected the synthesis of a previously undescribed system, 4-oxo-1,2,4-triazino [4,5-*a*] benzimidazole (I), and some of its derivatives.



The reaction of 2-benzimidazolecarboxyhydrazide (II) with an excess of orthoformic ester at 170–220°C gave I, a colorless crystalline substance with decomp. p. 336° C (from DMFA). Yield 80% IR spectrum (in paraffin oil): ν_{CO} 1680 cm^{-1}, ν_{NH} 3200 cm^{-1}. Found, %: C 57.83; H 3.45; N 30.46. Calculated for $C_9H_6N_4O$, %: C 58.05; H 3.24; N 30.10. When II was boiled with acetic anhydride, the 1-methyl derivative of I (III) was obtained with mp 276° C (from 50% ethanol). Found, %; C 60.61; H 4.39; N 28.01. Calculated for $C_{10}H_8N_4O$, %: C 60.44; H 4.03; N 27.98. When I was alkylated with the appropriate alkyl halides in an ethanolic solution of sodium ethoxide, the 3-methyl- and 3-ethyl derivatives of I (IV and V) were obtained. IV. Decomp. p. 310° C (from 50% DMFA). Found, %: