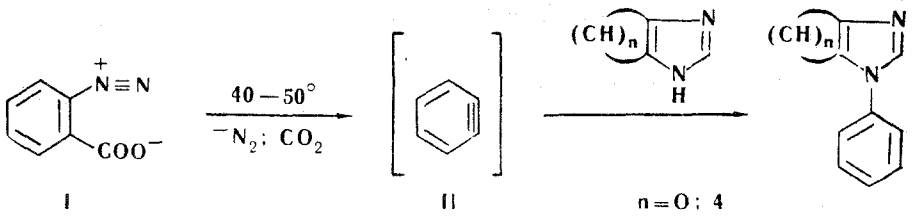
and benzimidazole. The generating source of II in the present work was the readily accessible o-diazobenzcarboxylate I, which undergoes mild thermal decomposition to carbon dioxide, nitrogen, and benzyne [2]




I II

A dioxane solution of the heterocyclic compound plus a slight excess of I was stirred at 40°–50° C for 50–60 hr. Then the precipitate, sparingly soluble in water and organic solvents (apparently a polymer mixture) was filtered off, and the solvent distilled off from the filtrate. The N-phenyl derivative formed was extracted from the residue with ether, and isolated as its picrate. Yield of 1-phenyl derivative of imidazole (picrate mp 151°–152° C, ex water), and benzimidazole (picrate mp 181° C, ex EtOH), 21 and 29%, respectively. Replacement of dioxane by benzene recommended in the literature [2], cuts yield and reproducibility, possibly because benzene is not indifferent towards II [3].

An attempt to arylate imidazole and benzimidazole with bromobenzene in liquid ammonia in the presence of potassamide, (when bromobenzene initially gives benzyne [4]) was unsuccessful.

The new method of arylation may be suitable for introducing aryl groups into compounds with groups which are unstable under the drastic conditions of the Ullman-Goldberg reaction.

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7 September 1965

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UDC 547.853 + 547.466

# N-(2-ETHYLTHIO-5-FLUOROPYRIMIDYL-4) AMINO ACIDS

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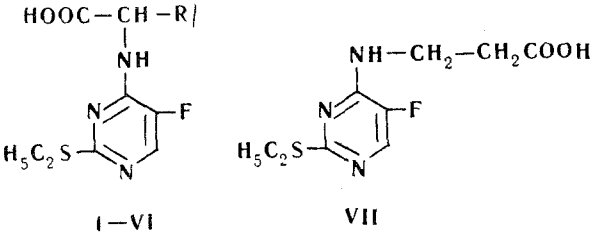
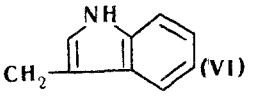
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 3, pp. 474–475, 1966

Continuing research on (5-fluoropyrimidyl-4) amino acids [1], we have prepared hitherto unknown N-(2-ethylthio-5-fluoropyrimidyl) amino acids (I–VIII), by reacting a 2-ethylthio-4-chloro-5-fluoroacyl with amino acids:



I–VI VII

R=H (I), $CH(CH_3)_2$ (II), $CH_2CH(CH_3)_2$ (III), $CH_2CH_2SCH_3$ (IV), $CH_2C_6H_5$ (V) and



I–VII are colorless crystalline compounds. Their physical constants, analytical data, and yields are given in the table.

N-(2-Ethylthio-5-fluoropyrimidyl-4) amino Acids

| Compound no. | Mp °C | Formula | Found, % | | | Calculated, % | | | $R_f$ in the system | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | C | H | N | *n*-$C_4H_9OH$—$CH_3CO_2H$—$H_2O$ 4 : 1 : 5 | *iso*-$C_3H_7OH$—$H_4OH$—$H_2O$ 14 : 1 : 5 | |
| I | 215 | $C_8H_{10}F_1N_3O_2S_1$ | 41.97 | 4.45 | 18.13 | 41.64 | 4.33 | 18.22 | — | 0.88 | 70 |
| II | 174 | $C_{11}H_{16}F_1N_3O_2S_1$ | 48.24 | 5.85 | 15.33 | 48.33 | 5.86 | 15.12 | 0.85* | 0.82 | 45 |
| III | 177 | $C_{12}H_{18}F_1N_3O_2S_1$ | 50.41 | 6.21 | 14.32 | 50.10 | 6.27 | 14.63 | 0.95 | 0.86 | 73 |
| IV | 173 | $C_{11}H_{16}F_1N_3O_2S_2$ | 43.42 | 5.57 | 13.63 | 43.27 | 5.24 | 13.27 | 0.84* | 0.90 | 62 |
| V | 186 | $C_{15}H_{16}F_1N_3O_2S_1$ | 56.37 | 5.58 | 13.05 | 56.07 | 4.98 | 13.08 | 0.85* | 0.92 | 67 |
| VI | 198 | $C_{17}H_{17}F_1N_4O_2S_1$ | 56.42 | 5.48 | 15.70 | 56.32 | 5.27 | 16.00 | 0.94 | 0.87 | 69 |
| VII | 141 | $C_9H_{12}F_1N_3O_2S_1$ | 44.11 | 4.43 | 17.34 | 44.08 | 4.89 | 17.14 | 0.89 | 0.90 | 52 |

* n-$C_4H_9OH$—$CH_3CO_2H$—$G_2O$ = 9 : 1 : 1.

The chemical and biological properties of I–VII are under investigation.

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28 September 1965

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