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Synthesis of 6-Acyl-7-aryl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylic Acids and Their Methyl Esters

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Abstract—6-Acyl-7-aryl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylic acids and methyl 6-acyl-7-aryl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylates were synthesized by fusion of 4-aryl-2,4-dioxobutanoic acids and their methyl esters, respectively, with 1*H*-tetrazol-5-amine and aromatic aldehydes. The reaction of methyl 2,4-dioxopentanoate with 1*H*-tetrazol-5-amine and 2-fluorobenzaldehyde in boiling acetic acid gave methyl 6-acetyl-5-hydroxy-7-(2-fluorophenyl)-4,5,6,7-tetrahydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylate.

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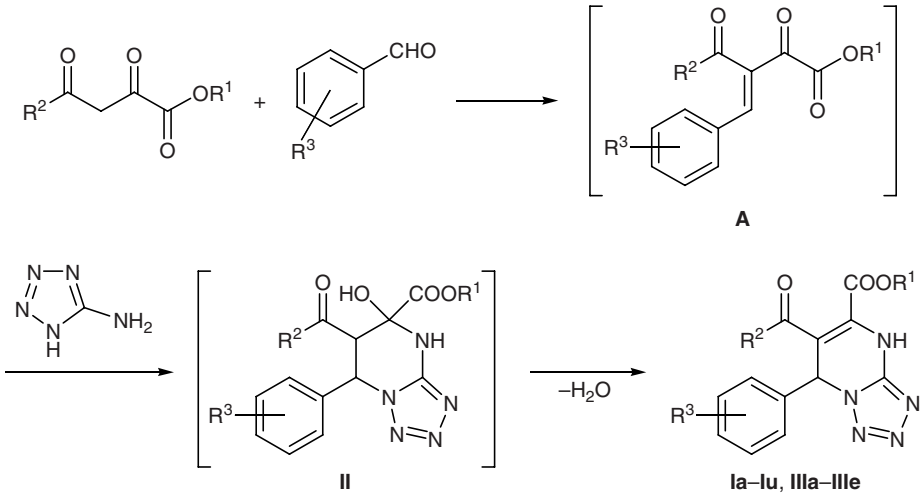
We previously showed that acylpyruvic acid esters react with aromatic aldehydes and 5-aminotetrazole [1] or 3-amino-1,2,4-triazole [2] to give methyl 6-acyl-7-aryl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylates and methyl 6-acyl-7-aryl-4,7-dihydro[1,2,4]triazolo[1,5-*a*]pyrimidine-5-carboxylates, respectively. Reactions of acylpyruvic acid esters with 5-amino-1,2,4-triazole [3], 3-amino-4,5-dihydropyrazol-5-one [4], 5-aminopyrazole [5], and 6-aminothiouracil [6] lead to the formation of a pyrimidine ring fused to the corresponding five- or six-membered heterocyclic system. It is also known that 4-acyl-5-aryl-1-hetarylpyrrolidine-2,3-diones are formed by reaction of acylpyruvic acid esters with a mixture of an aromatic aldehyde and 2-aminopyridine [7] or 4-amino-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (4-aminoantipyrine) [8].

With a view to synthesize new fused heterocyclic compounds we examined reactions of acylpyruvic acids and their methyl esters with 5-aminotetrazole and aromatic or heteroaromatic aldehydes. Fusion of methyl 4-aryl-2,4-dioxobutanoates or methyl 2,4-dioxopentanoate with a mixture of 1*H*-tetrazol-5-amine and aromatic aldehyde at 110–150°C gave the corresponding methyl 6-acyl-7-aryl-4,7-dihydrotetrazolo[1,5-*a*]-pyrimidine-5-carboxylates **Ia**–**Iu** (Scheme 1). Compounds **Ia**–**Iu** were isolated as colorless or colored crystalline substances; they are readily soluble in DMSO and DMF, soluble in ethanol, acetic acid, and dioxane on heating, and insoluble in water. The ^{1}H NMR spectra of **Ia**–**Iu** contain a three-proton singlet at δ 3.27–3.90 ppm from the ester methyl group, a singlet at δ 6.70–7.28 ppm from 7-H, a number of signals in the region δ 7.11–8.02 ppm from the aromatic protons, and a singlet at δ 11.10–12.19 ppm from the NH proton in position *4* of the heteroring. Compounds **Im**–**Iu** also displayed in the spectrum a three-proton singlet at δ 1.97–2.02 ppm from the acetyl group on C^6. In the IR spectra of **Ia**–**Iu** we observed absorption bands belonging to the ester carbonyl group (1725–1748 cm^{-1}), conjugated carbonyl group (C^6C=O, 1640–1709 cm^{-1}), and NH bond (3103–3169 cm^{-1}). The lower yields of compounds **Im**–**Iu** are likely to result from lower stability of methyl 2,4-dioxopentanoate as compared to methyl 4-aryl-2,4-dioxobutanoates.

Presumably, dioxo ester initially reacts with aromatic aldehyde to give unsaturated intermediate **A**, and the subsequent addition of 1*H*-tetrazol-5-amine at the double bond is accompanied by pyrimidine ring closure with formation of compounds **Ia**–**Iu**. This reaction scheme is confirmed by the fact that heating of a mixture of methyl 2,4-dioxopentanoate, 1*H*-tetrazol-5-amine, and 2-fluorobenzaldehyde in boiling acetic acid leads to the formation of methyl 6-acetyl-7-(2-fluorophenyl)-5-hydroxy-4,5,6,7-tetrahydrotetrazolo-[1,5-*a*]pyrimidine-5-carboxylate (**II**). Prolonged heating of compound **II** in acetic acid (2 h) resulted in its dehydration to compound (**Ir**). The dehydration prod-

Scheme 1.



I, R^1 = Me, R^2 = Ph (**a**–**c**), 4-FC_6H_4 (**d**–**f**), 4-ClC_6H_4 (**g**–**i**), 4-BrC_6H_4 (**j**–**l**); R^3 = H (**a**, **d**, **i**, **m**), 4-Cl (**b**, **h**, **n**), 3-F (**c**, **s**), 2-MeO (**e**), 3-MeO (**f**), 4-*t*-Bu (**g**), 4-*i*-Pr (**j**). 4-F (**k**), 4-MeO (**l**, **p**), 4-Br (**o**), 4-Me (**q**), 2-F (**r**), 3-O_2N (**t**), 4-O_2N (**u**); **II**, R^1 = R^2 = Me, R^3 = 2-F; **III**, R^1 = H, Ar = Ph (**a**, **c**, **d**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**e**); R^3 = H (**c**, **e**), 4-Cl (**d**), $R^3C_6H_4$ = pyridin-3-yl (**a**, **b**).

uct was identified by comparison with an authentic sample (no depression of the meting point was observed on mixing). Compound **II** is a colorless crystalline substance which is readily soluble in DMSO and DMF, soluble in ethanol and acetic acid on heating, and insoluble in water. Apart from signals typical of compounds **Ia**–**Iu**, the ^{1}H NMR spectrum of **II** contained singlets from the 6-H and OH protons at δ 3.65 and 7.09 ppm, respectively. In the IR spectrum of **II**, stretching vibrations of the ester and ketone carbonyl groups appeared at 1722 and 1629 cm^{-1}, respectively, and vibrations of the N–H and O–H bonds gave rise to absorption at 3294 cm^{-1}.

By fusion of methyl 4-aryl-2,4-dioxobutanoates with 1*H*-tetrazol-5-amine and pyridine-3-carboxaldehyde at 110–130°C we obtained 6-aroyl-7-(pyridin-3-yl)-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylic acids **IIIa** and **IIIb**. Obviously, the reaction is accompanied by elimination of methoxy group from the ester moiety, and the pyridine nitrogen atom acts as base catalyst in the hydrolysis. 6-Aroyl-7-aryl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylic acids **IIIc**–**IIIe** were synthesized by fusion at 120–150°C of the corresponding 4-aryl-2,4-dioxobutanoic acids with 1*H*-tetrazol-5-amine and aromatic aldehydes. Compounds **IIIa**–**IIIe** are colorless or colored crystalline substances, which are soluble in DMF, DMSO, and acetic acid, poorly soluble in alcohol, and insoluble in water. They give rise to a dark green color upon treatment with an alcoholic solution of iron(III) chloride.

In the ^{1}H NMR spectra of **IIIa**–**IIIe**, the 7-H signal appeared as a singlet at δ 6.72–7.07 ppm, aromatic protons resonated at δ 7.46–8.19 ppm, the NH singlet was observed at δ 11.13–11.37 ppm, and proton of the carboxy group gave a singlet at δ 13.75 (**IIIc**) or 14.20 ppm (**IIIe**). Compound **IIIb** also displayed in the spectrum a three-proton singlet at δ 2.31 ppm from the methyl group. The IR spectra of **IIIa**–**IIIe** contained absorption bands due to stretching vibrations of the ketone carbonyl group (1650–1680 cm^{-1}), carboxy group (C=O, 1710–1720 cm^{-1}; O–H, 3290–3320 cm^{-1}), and N–H bond (3110–3260 cm^{-1}).

EXPERIMENTAL

The IR spectra were recorded in mineral oil on a UR-20 instrument. The ^{1}H NMR spectra were measured on a Bruker DRX-500 spectrometer at 500.13 MHz from solutions in DMSO-d_6. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1320 mass spectrometer.

Methyl 6-benzoyl-7-phenyl-4,7-dihydrotetrazolo-[1,5-*a*]pyrimidine-5-carboxylate (Ia). A mixture of 0.01 mol of methyl 2,4-dioxo-4-phenylbutanoate, 0.01 mol of 1*H*-tetrazol-5-amine monohydrate, and 0.01 mol of benzaldehyde was heated at 110–150°C (metal bath) until gaseous products no longer evolved. The mixture was cooled and treated with ethanol, and the precipitate was filtered off and recrystallized from acetic acid. Yield 1.6 g (45%), mp 205–208°C. IR spectrum, ν, cm^{-1}: 1644 (C=O, ketone), 1725 (C=O,

ester), 3128 (N–H). ^{1}H NMR spectrum, δ, ppm: 3.30 s (3H, OCH_3), 6.80 s (1H, 7-H), 7.37 m (10H, H_{arom}), 11.40 s (1H, NH). Found, %: C 63.19; H 4.23; N 19.43. $C_{19}H_{15}N_5O_3$. Calculated, %: C 63.21; H 4.18; N 19.40.

Compounds **Ib**–**Iu** were synthesized in a similar way.

Methyl 6-benzoyl-7-(4-chlorophenyl)-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Ib). Yield 1.5 g (38%), mp 230–232°C. IR spectrum, ν, cm^{-1}: 1647 (C=O, ketone), 1731 (C=O, ester), 3156 (N–H). ^{1}H NMR spectrum, δ, ppm: 3.30 s (3H, OCH_3), 6.85 s (1H, 7-H), 7.46 m (9H, H_{arom}), 11.45 s (1H, NH). Found, %: C 57.76; H 3.53; N 17.71. $C_{19}H_{14}ClN_5O_3$. Calculated, %: C 57.72; H 3.57; N 17.69.

Methyl 6-benzoyl-7-(3-fluorophenyl)-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Ic). Yield 2.0 g (53%), mp 230–231°C. IR spectrum, ν, cm^{-1}: 1659 (C=O, ketone), 1740 (C=O, ester), 3147 (N–H). ^{1}H NMR spectrum, δ, ppm: 3.27 s (3H, CH_3), 6.93 s (1H, 7-H), 7.39 m (9H, H_{arom}), 11.61 s (1H, NH). Found, %: C 60.15; H 3.71; N 18.46. $C_{19}H_{14}FN_5O_3$. Calculated, %: C 60.14; H 3.69; N 18.44.

Methyl 6-(4-fluorobenzoyl)-7-phenyl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Id). Yield 3.4 g (91%), mp 206–208°C. IR spectrum, ν, cm^{-1}: 1640 (C=O, ketone), 1740 (C=O, ester), 3152 (N–H). ^{1}H NMR spectrum, δ, ppm: 3.30 s (3H, OCH_3), 6.80 s (1H, 7-H), 7.40 m (9H, H_{arom}), 11.40 s (1H, NH). Found, %: C 60.14; H 3.72; N 18.47. $C_{19}H_{14}FN_5O_3$. Calculated, %: C 60.15; H 3.68; N 18.44.

Methyl 6-(4-fluorobenzoyl)-7-(2-methoxyphenyl)-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Ie). Yield 3.2 g (78%), mp 227–229°C. IR spectrum, ν, cm^{-1}: 1650 (C=O, ketone), 1737 (C=O, ester), 3143 (N–H). ^{1}H NMR spectrum, δ, ppm: 3.29 s (3H, $COOCH_3$), 3.54 s (3H, OCH_3), 6.79 s (1H, 7-H), 7.30 m (8H, H_{arom}), 11.10 s (1H, NH). Found, %: C 58.72; H 3.94; N 17.12. $C_{20}H_{16}FN_5O_4$. Calculated, %: C 58.70; H 3.98; N 17.14.

Methyl 6-(4-fluorobenzoyl)-7-(3-methoxyphenyl)-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylate (If). Yield 2.8 g (70%), mp 221–223°C. IR spectrum, ν, cm^{-1}: 1647 (C=O, ketone), 1750 (C=O, ester), 3150 (N–H). ^{1}H NMR spectrum, δ, ppm: 3.29 s (3H, $COOCH_3$), 3.58 s (3H, OCH_3), 6.70 s (1H, 7-H), 7.11 m (8H, H_{arom}), 11.34 s (1H, NH). Found, %: C 58.71; H 3.93; N 17.13. $C_{20}H_{16}FN_5O_4$. Calculated, %: C 58.72; H 3.98; N 17.12.

Methyl 7-(4-*tert*-butylphenyl)-6-(4-chlorobenzoyl)-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Ig). Yield 1.9 g (42%), mp 231–232°C. IR spectrum, ν, cm^{-1}: 1662 (C=O, ketone), 1737 (C=O, ester), 3152 (N–H). ^{1}H NMR spectrum, δ, ppm: 1.19 s (9H, *t*-Bu), 3.38 s (3H, OCH_3), 6.81 s (1H, 7-H), 7.41 m (8H, H_{arom}), 11.53 s (1H, NH). Found, %: C 61.19; H 4.85; N 15.43. $C_{23}H_{22}ClN_5O_3$. Calculated, %: C 61.24; H 4.91; N 15.52.

Methyl 6-(4-chlorobenzoyl)-7-(4-chlorophenyl)-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Ih). Yield 2.9 g (67%), mp 225–227°C. IR spectrum, ν, cm^{-1}: 1655 (C=O, ketone), 1737 (C=O, ester), 3152 (N–H). ^{1}H NMR spectrum, δ, ppm: 3.40 s (3H, OCH_3), 6.80 s (1H, 7-H), 7.46 m (8H, H_{arom}), 11.45 s (1H, NH). Found, %: C 53.10; H 3.10; N 16.33. $C_{19}H_{13}Cl_2N_5O_3$. Calculated, %: C 53.06; H 3.04; N 16.28.

Methyl 6-(4-chlorobenzoyl)-7-phenyl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Ii). Yield 2.9 g (73%), mp 242–243°C. IR spectrum, ν, cm^{-1}: 1641 (C=O, ketone), 1743 (C=O, ester), 3152 (N–H). ^{1}H NMR spectrum, δ, ppm: 3.34 s (3H, OCH_3), 6.82 s (1H, 7-H), 7.50 m (9H, H_{arom}), 11.58 s (1H, NH). Found, %: C 57.76; H 3.59; N 17.72. $C_{19}H_{14}ClN_5O_3$. Calculated, %: C 57.72; H 3.57; N 17.69.

Methyl 6-(4-bromobenzoyl)-7-(4-isopropylphenyl)-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Ij). Yield 3.3 g (68%), mp 224–225°C. IR spectrum, ν, cm^{-1}: 1640 (C=O, ketone), 1737 (C=O, ester), 3123 (N–H). ^{1}H NMR spectrum, δ, ppm: 1.15 (7H, Pr-*i*), 3.45 s (3H, OCH_3), 6.72 s (1H, 7-H), 7.30 m (8H, H_{arom}), 11.30 s (1H, NH). Found, %: C 54.75; H 4.14; N 14.57. $C_{22}H_{20}BrN_5O_3$. Calculated, %: C 54.81; H 4.18; N 14.53.

Methyl 6-(4-bromobenzoyl)-7-(4-fluorophenyl)-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Ik). Yield 2.5 g (58%), mp 234–236°C. IR spectrum, ν, cm^{-1}: 1644 (C=O, ketone), 1743 (C=O, ester), 3177 (N–H). ^{1}H NMR spectrum, δ, ppm: 3.40 s (3H, OCH_3), 6.80 s (1H, 7-H), 7.30 m (8H, H_{arom}), 11.40 s (1H, NH). Found, %: C 53.17; H 3.04; N 9.79. $C_{19}H_{13}BrFN_3O_3$. Calculated, %: C 53.18; H 3.02; N 9.78.

Methyl 6-(4-bromobenzoyl)-7-(4-methoxyphenyl)-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Il). Yield 1.9 g (43%), mp 218–220°C. IR spectrum, ν, cm^{-1}: 1653 (C=O, ketone), 1740 (C=O, ester), 3152 (N–H). ^{1}H NMR spectrum, δ, ppm: 3.40 s (3H, $COOCH_3$), 3.72 s (3H, OCH_3), 6.71 s (1H, 7-H), 7.47 m (8H, H_{arom}), 11.35 s (1H, NH). Found, %:

C 51.62; H 3.64; N 15.84. $C_{19}H_{16}BrN_5O_3$. Calculated, %: C 51.60; H 3.68; N 15.81.

Methyl 6-acetyl-7-phenyl-4,7-dihydrotetrazolo-[1,5-*a*]pyrimidine-5-carboxylate (Im). Yield 1.7 g (57%), mp 212–214°C. IR spectrum, ν, cm^{-1}: 1657 (C=O, ketone), 1736 (C=O, ester), 3152 (N–H). ^1H NMR spectrum, δ, ppm: 1.98 s (3H, CH_3CO), 3.85 s (3H, OCH_3), 7.09 s (1H, 7-H), 7.42 m (5H, H_{arom}), 12.13 s (1H, NH). Found, %: C 56.30; H 4.42; N 23.38. $C_{14}H_{13}N_5O_3$. Calculated, %: C 56.23; H 4.38; N 23.42.

Methyl 6-acetyl-7-(4-chlorophenyl)-4,7-dihydro-tetrazolo[1,5-*a*]pyrimidine-5-carboxylate (In). Yield 0.7 g (22%), mp 224–226°C. IR spectrum, ν, cm^{-1}: 1709 (C=O, ketone), 1748 (C=O, ester), 3120 (N–H). ^1H NMR spectrum, δ, ppm: 2.00 s (3H, CH_3CO), 3.86 s (3H, OCH_3), 7.13 s (1H, 7-H), 7.49 m (4H, H_{arom}), 12.18 s (1H, NH). Found, %: C 50.44; H 3.60; N 21.09. $C_{14}H_{12}ClN_5O_3$. Calculated, %: C 50.49; H 3.63; N 21.00.

Methyl 6-acetyl-7-(4-bromophenyl)-4,7-dihydro-tetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Io). Yield 0.8 g (22%), mp 219–221°C. IR spectrum, ν, cm^{-1}: 1709 (C=O, ketone), 1743 (C=O, ester), 3162 (N–H). ^1H NMR spectrum, δ, ppm: 2.00 s (3H, CH_3CO), 3.85 s (3H, OCH_3), 7.09 s (1H, 7-H), 7.52 m (4H, H_{arom}), 12.15 s (1H, NH). Found, %: C 44.53; H 3.27; N 18.47. $C_{14}H_{12}BrN_5O_3$. Calculated, %: C 44.48; H 3.20; N 18.52.

Methyl 6-acetyl-7-(4-methoxyphenyl)-4,7-dihy-drotetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Ip). Yield 0.7 g (21%), mp 222–224°C. IR spectrum, ν, cm^{-1}: 1700 (C=O, ketone), 1745 (C=O, ester), 3169 (N–H). ^1H NMR spectrum, δ, ppm: 1.97 s (3H, CH_3CO), 3.65 s (3H, $COOCH_3$), 3.72 s (3H, OCH_3), 7.03 s (1H, 7-H), 7.35 m (4H, H_{arom}), 12.00 s (1H, NH). Found, %: C 54.69; H 4.48; N 21.18. $C_{15}H_{15}N_5O_4$. Calculated, %: C 54.75; H 4.59; N 21.28.

Methyl 6-acetyl-7-(4-methylphenyl)-4,7-dihydro-tetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Iq). Yield 2.8 g (89%), mp 229–231°C. IR spectrum, ν, cm^{-1}: 1696 (C=O, ketone), 1740 (C=O, ester), 3152 (N–H). ^1H NMR spectrum, δ, ppm: 1.97 s (3H, CH_3CO), 2.28 s (3H, CH_3), 3.84 s (3H, OCH_3), 7.04 s (1H, 7-H), 7.27 m (4H, H_{arom}), 12.08 s (1H, NH). Found, %: C 54.69; H 4.82; N 22.38. $C_{15}H_{15}N_5O_3$. Calculated, %: C 57.50; H 4.84; N 22.36.

Methyl 6-acetyl-7-(2-fluorophenyl)-4,7-dihydro-tetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Ir). Yield 0.7 g (22%), mp 210–212°C. IR spectrum, ν, cm^{-1}: 1671 (C=O, ketone), 1740 (C=O, ester), 3132 (N–H). ^1H NMR spectrum, δ, ppm: 2.03 s (3H, CH_3CO), 3.86 s (3H, OCH_3), 7.26 s (1H, 7-H), 7.40 m (4H, H_{arom}), 12.19 s (1H, NH). Found, %: C 53.05; H 3.83; N 22.11. $C_{14}H_{12}FN_5O_3$. Calculated, %: C 53.04; H 3.81; N 22.09.

Methyl 6-acetyl-7-(3-fluorophenyl)-4,7-dihydro-tetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Is). Yield 0.9 g (30%), mp 221–223°C. IR spectrum, ν, cm^{-1}: 1685 (C=O, ketone), 1735 (C=O, ester), 3165 (N–H). ^1H NMR spectrum, δ, ppm: 2.01 s (3H, CH_3CO), 3.87 s (3H, OCH_3), 7.13 s (1H, 7-H), 7.38 m (4H, H_{arom}), 12.19 s (1H, NH). Found, %: C 53.04; H 3.81; N 22.10. $C_{14}H_{12}FN_5O_3$. Calculated, %: C 53.05; H 3.83; N 22.11.

Methyl 6-acetyl-7-(3-nitrophenyl)-4,7-dihydro-tetrazolo[1,5-*a*]pyrimidine-5-carboxylate (It). Yield 1.0 g (29%), mp 208–210°C. IR spectrum, ν, cm^{-1}: 1692 (C=O, ketone), 1743 (C=O, ester), 3150 (N–H). ^1H NMR spectrum, δ, ppm: 2.02 s (3H, CH_3CO), 3.90 s (3H, OCH_3), 7.28 s (1H, 7-H), 8.02 m (4H, H_{arom}), 12.17 s (1H, NH). Found, %: C 48.82; H 3.51; N 24.39. $C_{14}H_{12}N_6O_5$. Calculated, %: C 48.83; H 3.52; N 24.41.

Methyl 6-acetyl-7-(4-nitrophenyl)-4,7-dihydro-tetrazolo[1,5-*a*]pyrimidine-5-carboxylate (Iu). Yield 1.0 g (31%), mp 221–223°C. IR spectrum, ν, cm^{-1}: 1685 (C=O, ketone), 1743 (C=O, ester), 3103 (N–H). ^1H NMR spectrum, δ, ppm: 2.02 s (3H, CH_3CO), 3.89 s (3H, OCH_3), 7.07 s (1H, OH), 7.21 s (1H, 7-H), 8.00 m (4H, H_{arom}), 12.15 s (1H, NH). Found, %: C 48.84; H 3.51; N 24.38. $C_{14}H_{12}N_6O_5$. Calculated, %: C 48.83; H 3.51; N 24.42.

Methyl 6-acetyl-7-(2-fluorophenyl)-5-hydroxy-4,5,6,7-tetrahydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylate (II). A mixture of 0.01 mol of methyl 2,4-dioxopentanoate, 0.01 mol of 2-fluorobenzaldehyde, and 0.01 mol of 1*H*-tetrazol-5-amine in 10 ml of acetic acid was heated for 30 min on a boiling water bath. The mixture was kept for 24 h at room temperature, and the precipitate was filtered off and recrystallized from ethanol. Yield 0.5 g (16%), mp 163–165°C. IR spectrum, ν, cm^{-1}: 1629 (C=O, ketone), 1722 (C=O, ester), 3294 (N–H, O–H). ^1H NMR spectrum, δ, ppm: 2.00 s (3H, CH_3CO), 3.65 s (1H, 6-H), 3.75 s (3H, OCH_3), 7.09 s (1H, OH), 5.80 s (1H, 7-H), 7.35 m (4H, H_{arom}), 9.07 s (1H, NH). Found, %: C 50.30; H 3.32; N 20.92. $C_{14}H_{14}FN_5O_4$. Calculated, %: C 50.34; H 3.92; N 20.97.

6-Benzoyl-7-(pyridin-3-yl)-4,7-dihydrotetrazolo-[1,5-*a*]pyrimidine-5-carboxylic acid (IIIa). A mixture of 0.01 mol of 2,4-dioxo-4-phenylbutanoate, 0.01 mol of 1*H*-tetrazol-5-amine monohydrate, and 0.01 mol of pyridine-3-carbaldehyde was fused at 110–150°C on a metal bath until gaseous products no longer evolved. The melt was cooled and treated with ethanol, and the precipitate was filtered off and recrystallized from acetic acid. Yield 0.8 g (22%), mp 224–226°C. IR spectrum, ν, cm^{-1}: 1720, 3320 (COOH); 1650 (C=O, ketone); 3105 (N–H). ^{1}H NMR spectrum, δ, ppm: 6.90 s (1H, 7-H), 8.19 m (9H, H_{arom}), 11.33 s (1H, NH). Found, %: C 58.57; H 3.45; N 24.10. $C_{17}H_{12}N_6O_3$. Calculated, %: C 58.60; H 3.48; N 24.12.

Compounds **IIIb**–**IIIe** were synthesized in a similar way.

6-(4-Methylbenzoyl)-7-(pyridin-3-yl)-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylic acid (IIIb). Yield 1.9 g (47%), mp 198–200°C. IR spectrum, ν, cm^{-1}: 1710, 3390 (COOH); 1660 (C=O, ketone), 3100 (N–H). ^{1}H NMR spectrum, δ, ppm: 2.31 s (3H, CH_3), 6.88 s (1H, 7-H), 7.79 m (8H, H_{arom}), 11.24 s (1H, NH). Found, %: C 62.95; H 4.01; N 20.97. $C_{21}H_{14}N_6O_3$. Calculated, %: C 62.97; H 4.03; N 20.99.

6-Benzoyl-7-phenyl-4,7-dihydrotetrazolo[1,5-*a*]-pyrimidine-5-carboxylic acid (IIIc). Yield 1.2 g (43%), mp 206–208°C. IR spectrum, ν, cm^{-1}: 1770, 3290 (COOH); 1660 (C=O, ketone); 3260 (N–H). ^{1}H NMR spectrum, δ, ppm: 6.72 s (1H, 7-H), 7.48 m (10H, H_{arom}), 11.13 s (1H, NH), 13.75 s (1H, OH). Found, %: C 62.26; H 3.74; N 20.90. $C_{18}H_{13}N_5O_3$. Calculated, %: C 62.20; H 3.77; N 18.38.

6-Benzoyl-7-(4-chlorophenyl)-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylic acid (IIId). Yield 1.3 g (33%), mp 213–214°C. IR spectrum, ν, cm^{-1}: 1710, 3290 (COOH); 1680 (C=O); 3210 (N–H). ^{1}H NMR spectrum, δ, ppm: 6.84 s (1H, 7-H), 7.46 m (9H, H_{arom}), 11.26 s (1H, NH), 14.20 (1H, OH). Found, %: C 57.17; H 3.23; N 18.35. $C_{18}H_{12}ClN_5O_3$. Calculated, %: C 57.20; H 3.17; N 18.38.

6-(4-Chlorobenzoyl)-7-phenyl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-5-carboxylic acid (IIIe). Yield 1.3 g (35%), mp 204–206°C. IR spectrum, ν, cm^{-1}: 1710, 3290 (COOH); 1660 (C=O); 3180 (N–H). ^{1}H NMR spectrum, δ, ppm: 7.07 s (1H, 7-H), 7.75 m (9H, H_{arom}), 11.37 s (1H, NH). Found, %: C 57.18; H 3.22; N 18.34. $C_{18}H_{12}ClN_5O_3$. Calculated, %: C 57.19; H 3.19; N 18.37.

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