Synthesis and Growth Regulatory Activity of Pyrazolesulfanyl- and Isoxazolesulfanyl-1*H*-[1,2,4]triazoles and Their Azinyl Derivatives

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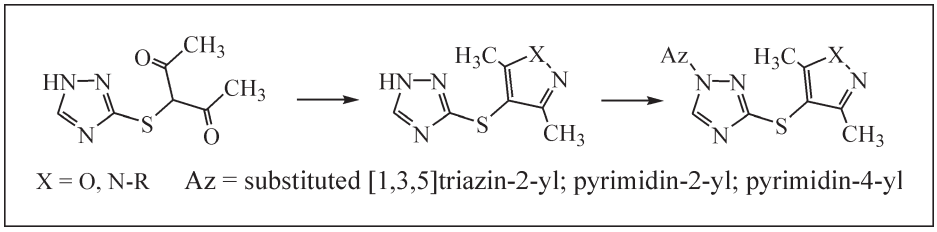

By cyclocondensation of 3-(1*H*-[1,2,4]triazol-3-ylsulfanyl)-pentane-2,4-dion with hydroxylamine, hydrazine, methylhidrazine, and arylsulfonyl-hydrazides, the 3-(3,5-dimethyl-isoxazol-4-ylsulfanyl)-1*H*-[1,2,4]triazole (**2**) and 3-(3,5-dimethyl-1-R-pyrazol-4-ylsulfanyl)-1*H*-[1,2,4]triazoles (**3a–d**) are synthesized. Under the action of quaternary ammonium salts of azines with limited heating in acetone they form a series of compounds (**4a–h**), which molecules simultaneously contain three different heterocyclic rings. Structures of compounds were confirmed by ^{1}H and ^{13}C NMR, MS, and elemental analysis. The plants growth regulatory activities of compounds **4a–h** were investigated. Data of biological tests testify that these compounds can be of interest to search for new growth stimulators.

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INTRODUCTION

Among the 1,2,4-triazole derivatives the large number of fungicides, herbicides, insecticides, and plant growth stimulators are known that are widely used in agriculture [1]. The majority of these compounds contain in their molecules a triazole cycle that directly or through different atomic groups is connected with the substituted phenyl ring. At the same time, there is a significant interest in searching for potential pesticides among the compounds, in molecules of which the triazole ring is connected with other heterocycles directly or through the heteroatom. Earlier, by regioselective alkylation and acylation in the position 1 of 3-S-substituted 1*H*-[1,2,4] triazoles, we had synthesized a new series of corresponding azinyl derivatives [2,3].

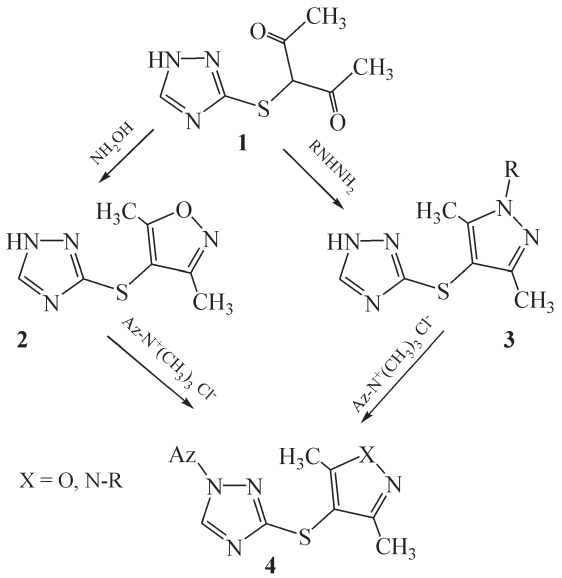
Among the pyrazole and isoxazole derivatives the substances with herbicidal [4–14], fungicidal [15–20], and insecticidal [21–25] activity were also revealed. However, the number of these preparations is incomparably smaller than the chemical means of plant protection with triazole, triazine, pyrimidine, thiadiazole, and thiazole cycles [1]. Therefore, the purpose of the present research was to synthesize new compounds that contain pyrazole or isoxazole cycles, connected with triazole ring through a sulfur atom, and further substitution in the position 1 of triazoles to obtain corresponding azinyl-derivatives.

RESULTS AND DISCUSSION

As the initial compound, we used previously synthesized 3-(1*H*-[1,2,4]triazole-3-ylsulfanyl)-pentane-2,4-dione **1** [2] that under the action of hydroxylamine and different hydrazides undergoes a cyclocondensation, and a new series of compounds **2** and **3** are formed (Scheme 1). The mentioned substances are obtained in sufficiently high yields in the aqueous medium at heating up to 80°C.

In triazole cycle of the synthesized compounds **2** and **3** the process of the prototropic tautomerism can occur. Usually the proton exchange between the heteroatoms proceeds ''fast'' (in comparison with a temporary NMR-scale), so in spectra only the averaged signals from two tautomeric forms are observed. However, in ^{1}H NMR spectra of compounds **2** and **3** at room temperature two broadened signals are observed that belong to the protons for each NH and CH groups of heterocycle. During heating up to 60°C, when the speed of exchange between the

Scheme 1



tautomeric forms increases, the signals of the mentioned protons in pairs coalescence into the single peak.

The synthesized isoxazole- (**2**) and pyrazole- (**3**) derivatives under the action of substituted triazine(pyrimidine)-2-yl- (or 4-yl)-trimethyl-ammonium chlorides at limited heating in acetone form series of compounds (**4**) that contain in the molecules simultaneously three different heterocyclic rings (Scheme 1). Azinyl-trimethyl-ammonium chlorides were obtained by substitution of chlorine atoms in 2,4,6-trichloro-[1,3,5]azin. The stepwise substitution of the first two chlorine atoms proceeds smoothly, but the substitution of the third chlorine atom (including interaction with triazole cycle) is problematic. In such cases, we have proposed to use more electrophilic azinyl-trimethyl-ammonium chlorides, which are easily obtained by the interaction of trimethyl-amine with 4,6-substituted 2-chloro-azins [26,27].

In the case of compounds **4**, the basic question is at which position of triazole ring the heterylation reaction occurs. Value of 9.0–9.1 ppm for H-5 in ^{1}H NMR spectra allows excluding 2-N substitution [28], but do not make a choice between 1-N and 4-N substitutions. In some cases, by means of mass spectra a substitution position in triazole cycle can be established [29–31]. However, in mass spectra of synthesized compounds **4**, the molecular fragments, which allow answering this question, were not detected. For example, in mass spectra of compounds **4d** and **4g**, the major registered fragments are for **4d:** 318(M^+,100), 275(22), 165(21), 150(29), 123(54), 43(43) and for **4g**: 316(M^+,52), 283(11), 140(9), 109(100), 56(75), 43(32). For this reason, ^{13}C NMR spectra of some unsubstituted derivatives (**2,3**), final products (**4**), and corresponding methyl-sulfanyl derivatives were determined. The assignment of triazole carbon atoms was made by comparison of decoupled and proton-coupled spectra of these compounds. Chemical shifts of carbon atoms were compared with the corresponding data, given in [32]. In this article, it was established that if 1-N substitution take place, the chemical shifts of C_3 are in the range of 157.4–160.3 ppm, but in the case of 4-N-substitution, the peak of this carbon appears at 149.6–153.1 ppm. In ^{13}C NMR spectra of the synthesized compounds, the signal of C_3 carbon atom is observed in the range of 155.1–160.3 ppm. These data are in agreement with 1-N substitution in triazole cycle.

BIOLOGICAL ACTIVITY

For preliminary screening tests, the compounds **4a–h** were selected, and growth regulatory activity of their solutions in concentrations 25 and 50 mg/L was investigated on the swelling, growth, morphogenesis, and survivability of seeds and seedlings of dicotyledonous culture plant, French bean. The activity of these compounds was compared with heteroauxin activity. All investigated substances in a various degree had a stimulator activity (**4a**-10% compared with heteroauxin; **4b**-95%; **4c**-30%; **4d**-70%; **4e**-40%; **4f**-45%; **4g**-100%; **4h**-120%). These data testify the necessity of deeper researches of the growth regulatory activity among the investigated derivatives. One compound (**4h**) that surpasses heteroauxin on 20% was selected for field trials.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were determined by Varian Mercury-300 MHz spectrometer, in the mixture of solvents DMSO-d_6 and CCl_4 (1:3), using tetramethylsilane as internal standard. Mass-spectra were recorded on MX-1321A MS system (70 eV). The reaction course control and individuality of the obtained substances were checked by using the TLC method on ''Silufol UV-254'' plates and acetone-hexane mixture (2:1) as eluent. Melting points are uncorrected. Initial 3-(1*H*-[1,2,4]triazole-3-ylsulfanyl)-pentane-2,4-dione (**1**) was prepared as described in [2].

3-(3,5-Dimethyl-isoxazol-4-ylsulfanyl)-1*H*-[1,2,4]triazole (2). A mixture of compound **1** (2.0 g; 0.01 mol), hydroxylamine sulfate (0.9 g; 0.11 mol), and potassium carbonate (0.77 g; 0.11 mol) was heated at reflux over a steam bath for 1.5 h. The mixture was cooled and then the compound **2** was filtered off and recrystallized from water. The compound was obtained as white crystals; m.p. 138–139°C, yield: 1.78 g (91%). ^{1}H NMR: δ 2.22 (s, 3H, CH_3); 2.48 (s, 3H, CH_3); 8.12 (b.s, 1H, 5-H); 13.60 (b.s, 1H, NH). ^{13}C NMR: δ 9.9; 11.2; 102.2; 146.0 (C_5); 156.1 (C_3); 161.7; 173.0. MS (*m*/*z*) 196 (M^+). Anal. Calcd for $C_7H_8N_4OS$: C, 42.85; H, 4.11; N, 28.55; S, 16.34. Found: C, 42.55; H, 4.20; N, 28.65; S, 16.61.

3-(3,5-Dimethyl-1*H*-pyrazole-4-ylsulfanyl)-1*H*-[1,2,4]triazole (3a). The mixture of compound **1** (2.0 g; 0.01 mol) and 5 mL of 63% hydrazine hydrate was allowed to stand at 20°C for 24 h. The obtained transparent solution (pH > 9) was neutralized with acetic acid, filtered off and the filtration residue of compound **3a** was washed with 5 mL of H_2O, dried in the air and purified by boiling in toluene. The compound was obtained as white crystals; m.p. 218–220°C, yield: 1.48 g (76%). ^{1}H NMR (60°C): δ 2.21 [s, 6H, $(CH_3)_2$]; 8.15 (b.s, 1H, 5-H triazole); 13.30 and 13.62 (b.s, 1H, 1H, NH-pyrazole and NH-triazole). MS (*m/z*) 195 (M^+). Anal. Calcd for $C_7H_9N_5S$: C, 43.06; H, 4.65; N, 35.87; S, 16.42; Found: C, 43.24; H, 5.01; N, 35.67; S, 16.25.

3-(1,3,5-Trimethyl-1*H*-pyrazol-4-ylsulfanyl)-1*H*-[1,2,4]triazole (3b). At 0°C, 1.44 g (0.01 mol) of methylhydrazine sulfate was dissolved with continuous stirring in 20 mL of 10% sodium hydroxide solution. On reaching to 15°C, 0.01 mol of compound **1** was added by portions, then the temperature was raised up to 60°C and the mixture was allowed to stand for 1 h. The mixture was neutralized with acetic acid to pH 7, then filtered off and the residue of compound **3b** was washed with 5 mL of H_2O and dried in the air. Purified by recrystallization from toluene. The compound was obtained as white crystals; m.p. 158–160°C, yield: 1.78 g (85%). ^{1}H NMR (60°C): δ 2.13 (s, 3H, CH_3); 2.30 (s, 3H, CH_3); 3.73 (s, 3H, NCH_3); 7.93 (b.s, 1H, 5-H triazole); 13.40 (b.s, 1H, NH). ^{13}C NMR: δ 9.7; 11.7; 36.4; 100.6; 143.3; 146.8(C_5); 149.5; 156.7 (C_3). MS (*m/z*) 209 (M^+). Anal. Calcd for $C_8H_{11}N_5S$: C, 45.91; H, 5.30; N, 33.47; S, 15.32; Found: C, 45.70; H, 5.49; N, 33.63; S, 15.50.

3-[1-(Toluene-4-sulfonyl)-3,5-dimethyl-1*H*-pyrazol-4-ylsulfanyl]-1*H*-[1,2,4]-triazole (3c). The suspension of compound **1** (2.0 g; 0.01 mol) and para-toluenesulfonyl hydrazine (1.86 g; 0.01 mol) in 10 mL of H_2O was heated at 60°C for 3 h. The water was decanted, viscous oil processed with ice-cold water and the sediment of compound **3c** filtered off. Purified by recrystallization from benzene. The compound was obtained as white crystals; m.p. 150–152°C, yield: 3.07 g (88%). ^{1}H NMR (60°C): δ 2.20 (s, 3H, CH_3); 2.45 (s, 3H, CH_3-tolyl); 2.62 (s, 3H, CH_3); 7.36–7.85 (m, 4H, C_6H_4); 8.20 (b.s, 1H, 5-H triazole); 13.80 (b.s, 1H, NH). MS (*m/z*) 349 (M^+). Anal. Calcd for $C_{14}H_{15}N_5O_2S_2$: C, 48.12; H, 4.33; N, 20.04; S, 18.35; Found: C, 48.36; H, 4.60; N, 20.31; S, 18.49.

3-(1-Benzenesulfonyl-3,5-dimethyl-1*H*-pyrazol-4-ylsulfanyl)-1*H*-[1,2,4]triazole (3d). 3-(1-Benzenesulfonyl-3,5-dimethyl-1H-pyrazol-4-ylsulfanyl)-1H-[1,2,4]triazole (3d) was obtained according to the mentioned above description. Purified by recrystallization from benzene. The compound was obtained as white crystals; m.p. 130–132°C, yield: 2.95 g (88%). ^{1}H NMR (60°C): δ 2.18 (s, 3H, CH_3); 2.62 (s, 3H, CH_3); 7.58–8.00 (m, 5H, C_6H_5); 8.15 (b.s, 1H, 5-H triazole); 13.70 (b.s, 1H, NH). MS (*m/z*) 335 (M^+). Anal. Calcd for $C_{13}H_{13}N_5O_2S_2$: C, 46.55; H, 3.91; N, 20.88; S, 19.12; Found: C, 46.44; H, 4.17; N, 21.11; S, 19.40.

Synthesis of compounds 4a–h.

General procedure. Compound **2** (or **3**) (0.01 mol) was added with continuous stirring to suspension of 0.01 mol KOH in 20 mL of dry acetone. In an hour at 0°C, 0.01 mol of azinyltrimethylammonium chloride was added. The reaction mixture was stirred at 20°C for 5 h, then at 50–52°C for 2 h. The suspension was evaporated, the residue was washed with water, and then the compound **4** was filtered off and dried in the air.

1-(4,6-Bis-dimethylamino-[1,3,5]triazin-2-yl)-3-(3,5-dimethyl-isoxazol-4-yl-sulfanyl)-[1,2,4]-triazole (4a). Purified by recrystallization from benzene. The compound was obtained as white crystals; m.p. 167–169°C, yield 3.25 g (90%). ^{1}H NMR: δ 2.25 (s, 3H, CH_3); 2.50 (s, 3H, CH_3); 3.18 and 3.22 [s,s, 6H,6H, 4,6-$N(CH_3)_2$]; 9.08 (s, 1H, 5-H triazole). MS (*m/z*) 361 (M^+). Anal. Calcd for $C_{14}H_{19}N_9OS$: C, 46.52; H, 5.30; N, 34.88. S, 8.87; Found: C, 46.71; H, 5.22; N, 35.10; S, 9.11.

1-(4-Dimethylamino-6-morpholin-4-yl-[1,3,5]triazin-2-yl)-3-(3,5-dimethyl-isoxazol-4-ylsulfanyl)-[1,2,4]triazole (4b). Purified by boiling in benzene. The compound was obtained as white crystals; m.p. 226–228°C, yield: 3.22 g (80%). ^{1}H NMR: δ 2.20 (s, 3H, CH_3); 2.48 (s, 3H, CH_3); 3.18 and 3.23 [s,s, 3H,3H, $N(CH_3)_2$]; 3.60–3.70 [m, 4H, $O(CH_2)_2$]; 3.83 [b.m, 4H, $N(CH_2)_2$]; 9.06 (s, 1H, 5-H triazole). ^{13}C NMR: δ 9.6; 11.1; 35.7; 43.4; 65.6; 101.3; 145.8 (C_5); 159.4 (C_3); 159.9; 161.5; 164.3; 164.9; 173.0. MS (*m/z*) 403 (M^+). Anal. Calcd for $C_{16}H_{21}N_9O_2S$: C, 47.63; H, 5.25; N, 31.24; S, 7.95; Found: C, 47.86; H, 5.21; N, 31.48; S, 8.11.

1-(4-Methyl-6-amino-[1,3,5]triazin-2-yl)-3-(3,5-dimethyl-isoxazol-4-ylsulfanyl)-[1,2,4]-triazole (4c). Purified by boiling in benzene. The compound was obtained as white crystals; m.p. 240–242°C, yield: 2.0 g (66%). ^{1}H NMR: δ 2.19 (s, 3H, CH_3); 2.37 (s, 3H, 4-CH_3); 2.50 (s, 3H, CH_3); 6.40 (b.s, 2H, NH_2); 9.03 (s, 1H, 5-H triazole). MS (*m/z*) 304 (M^+). Anal. Calcd for $C_{11}H_{12}N_8OS$: C, 43.41; H, 3.97; N, 36.82; S, 10.54; Found: C, 43.13; H, 4.01; N, 36.61; S, 10.74.

1-(4-Methoxy-6-methyl-pyrimidin-2-yl)-3-(3,5-dimethyl-isoxazol-4-ylsulfanyl)-[1,2,4]-triazole (4d). Purified by recrystallization from the mixture of benzene:hexane (1:1). The compound was obtained as white crystals; m.p. 153–155°C, yield: 2.48 g (78%). ^{1}H NMR: δ 2.25 (s, 3H, CH_3); 2.48 (s, 3H, 4-CH_3); 2.55 (s, 3H, CH_3); 4.03 (s, 3H, CH_3); 6.62 (s, 1H, 5-H-pyrim.); 9.10 (s, 1H, 5-H triazole). ^{13}C NMR: δ 9.9; 11.3; 23.3; 54.4; 101.3; 105.2; 145.9 (C_3); 152.5; 160.3 (C_3); 161.8; 169.7; 170.8; 173.4. MS (*m/z*) 318 (M^+). Anal. Calcd for $C_{13}H_{14}N_6O_2S$: C, 49.05; H, 4.43; N, 26.40; S, 10.07; Found: C, 49.27; H, 4.65; N, 26.69; S, 10.29.

1-(4,6-Bis-dimethylamino-[1,3,5]triazin-2-yl)-3-(1,3,5-trimethyl-1H-pyrazol-4-ylsulfanyl)-[1,2,4]-triazole (4e). Purified by recrystallization from benzene. The compound was obtained as white crystals; m.p. 186–188°C, yield: 2.92 g (78%). ^{1}H NMR: δ 2.20 (s, 3H, CH_3); 2.33 (s, 3H, CH_3); 3.17 and 3.22 [s,s, 6H,6H, $N(CH_3)_2$]; 3.75 (s, 3H, NCH_3); 9.00 (s, 1H, 5-H triazole). ^{13}C NMR: δ 9.8; 11.8; 35.7; 36.4; 100.0; 143.4; 145.6(C_5); 149.7; 159.3(C_3); 161.9; 164.9. MS (*m/z*) 374 (M^+). Anal. Calcd for $C_{15}H_{22}N_{10}S$: C, 48.11; H, 5.92; N, 37.40; S, 8.56; Found: C, 47.84; H, 6.21; N, 37.20; S, 8.38.

1-(4-Dimethylamino-6-morpholin-4-yl-[1,3,5]triazin-2-yl)-3-(1,3,5-trimethyl-1H-pyrazol-4-ylsulfanyl)-[1,2,4]triazole (4f). Purified by recrystallization from benzene. The compound was obtained as white crystals; m.p. 152–154°C, yield: 3.75 g (90%). ^{1}H NMR: δ 2.20 (s, 3H, CH_3); 2.32 (s, 3H, CH_3); 3.17 and 3.23 [s,s, 3H,3H, $N(CH_3)_2$]; 3.63–3.70 [m, 4H, $O(CH_2)_2$]; 3.73 (s, 3H, NCH_3); 3.82 [b.m, 4H, $N(CH_2)_2$]; 9.00 (s, 1H, 5-H triazole). MS (*m/z*) 416 (M^+). Anal. Calcd for $C_{17}H_{24}N_{10}OS$: C, 49.02; H, 5.81; N, 33.63; S, 7.70; Found: C, 48.79; H, 6.03; N, 33.81; S, 7.93.

1-(2-Amino-6-methyl-pyrimidin-4-yl)-3-(1,3,5-trimethyl-1H-pyrazol-4-ylsulfanyl)-[1,2,4]triazole (4g). Purified by boiling in benzene. The compound was obtained as white crystals; mp

236–237°C, yield: 2.84 g (90%). ^{1}H NMR: δ 2.19 (s, 3H, CH_3); 2.32 (s, 3H, CH_3); 2.37 (s, 3H, 6-CH_3); 3.76 (s, 3H, NCH_3); 6.42 (b.s, 2H, NH_2); 6.72 (s, 1H, 5-H pyrim.); 8.97 (s, 1H, 5-H triazole). ^{13}C NMR: δ 9.8; 11.8; 23.85; 36.4; 96.1; 99.6; 143.2 (C_5); 143.5; 149.7; 155.1 (C_3); 162.3; 162.9; 171.1. MS (*m/z*) 316 (M^+). Anal. Calcd for $C_{13}H_{16}N_8S$: C, 49.35; H, 5.10; N, 35.42; S, 10.13; Found: C, 49.24; H, 5.31; N, 35.70; S, 10.17.

1-(4-Methoxy-6-methyl-pyrimidin-2-yl)-3-(1,3,5-trimethyl-1H-pyrazol-4-yl-sulfanyl)-[1,2,4]triazole (4h). Purified by recrystallization from the mixture of benzene:hexane(1:1). The compound was obtained as white crystals; m.p. 236–237°C, yield: 2.71 g (82%). ^{1}H NMR: δ 2.20 (s, 3H, CH_3); 2.35 (s, 3H, CH_3); 2.47 (s, 3H, 4-CH_3); 3.75 (s, 3H, NCH_3); 4.05 (s, 3H, OCH_3); 6.60 (s, 1H, 5-H pyrim.); 9.02 (s, 1H, 5-H triazole). MS (*m/z*) 331 (M^+). Anal. Calcd for $C_{14}H_{17}N_7OS$: C, 50.74; H, 5.17; N, 29.59; S, 9.68; Found: C, 50.85; H, 5.42; N, 29.92; S, 10.02.

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