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## Synthesis and Biological Evaluation of Novel Nonfused Heterocyclic Systems Derivatives Based On 5-(Alkylthio)-1, 3, 4-Thiadiazole-2(3H)-Thions

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**Abstract:** Convenient high yield methods for the synthesis of 33 novel 1, 3, 4-thiadiazolylthio-1,3,5-triazines and pyrimidines with various substituents are elaborated. The treatment of started 5-(alkylthio)-1,3,4-thiadiazole-2(3H)-thiones with 2,4-dichloro-6-alkyl(dialkyl)amino-1,3,5-triazines and 2,4-dichloro-6-methylpyrimidine led to 2-chloro substituted 4-((5-(alkylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(alkyl(dialkyl)amino)-1,3,5-triazines and 4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-methyl-pyrimidine. The latter with trimethylamine formed the corresponding (pyrimidin-2-yl)-trimethyl-ammonium chloride. The reaction of this salt with methyl 4-hydroxybenzoate yielded 2-(4-methoxycarbonyl-phenoxy)-4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-methyl-pyrimidine. The interaction of 2-chloro-4-((5-(alkylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(alkyl(dialkyl)amino)-1,3,5-triazines with thiourea and further treatment with KOH afforded 4-((5-(alkylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(alkyl(dialkyl)amino)-1,3,5-triazine-2-thiols via intermediate 4-((5-(alkylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(alkyl(dialkyl)amino)-1,3,5-triazin-2-yl carbamimidothioate hydrochlorides. These thiols were easily alkylated into the corresponding alkyl derivatives.

The hydrazinolysis of started 5-(alkylthio)-1,3,4-thiadiazole-2(3H)-thiones occurred very easy at room temperature, and corresponding 2-hydrazinyl substituted

derivatives were formed. Their cyclization with pentane-2,4-dione afforded 2-(3,5-dimethyl-1*H*-pyrazol-1-yl) substituted derivatives. At the same time the reaction of the same hydrazinyl derivatives with ethyl 3-oxobutanoate led to acyclic hydrazonobutanoates. The synthesized compounds have shown the pronounced plant growth stimulant properties. The most active compounds were selected for deeper laboratory study and further field trials.

**Keywords:** 5-(Alkylthio)-1,3,4-thiadiazole-2(3*H*)-thions, 1,3,4-Thiadiazolylthio-1,3,5-triazines, 1,3,4-Thiadiazolylthio-pyrimidines, Plant growth stimulant activity.

## INTRODUCTION

To increase the yield of crops, the intensive technologies based on the use of fertilizers and pesticides are used. Currently, there is no alternative for them, because the use of chemical means of plant protection is economically most effective. At the same time pesticides have two disadvantages, such as the appearance of harmful organisms resistance against the applied means, as well as the undesirable influence of pesticides on the environment. These two problems make necessary the continuously search for new physiologically active compounds. Indention

The arsenal of pesticides based on 1,3,4-thiadiazole is limited. There are known fungicides (etridiazole, saisentong, thiadiazole-copper, zinc-thiazole), herbicides of the urea series (buthiuron, ethidimuron, tebuthiuron, thiazafluron, thiadiazuron) and organophosphorus insecticides (athidathion, lythidathion, methidathion, prothidathion)<sup>1</sup>.

In the last two decades, the researches in the series of 1,3,4-thiadiazole derivatives are continued, and new compounds with fungicidal<sup>2-5</sup>, acaricidal<sup>6,7</sup> and herbicidal<sup>8,9</sup> activities were discovered. In these studies, mostly the functionalization of thiadiazole cycle was carried out. At the same time, there are no literature data on pesticidal activity of the heterocyclic systems with combination of thiadiazole ring with other pharmacophoric heterocycles in the same molecule, in particular, with pyrimidine or 1,3,5-triazine, which derivatives have the greatest application in agriculture. Among pyrimidine derivatives are well known fungicides, the herbicides of the series of pyrimidinediamines, pyrimidinylxy(thio)benzoic acids, pyrimidinylxybenzylamino benzoates and pyrimidinylsulfonylureas, pyrimidinamine insecticides, rodenticides and acaricides, pyrimidine organophosphate insecticides<sup>1</sup>. The compounds, based on 1,3,5-triazine and its halogen-, methoxy- and metylthio derivatives, substituted triazinones and 2,4-diones, more than ten triazinylsulfonylureas are also widely used as herbicides<sup>1</sup>.

The purpose of present research was the targeted synthesis of novel unfused heterocyclic systems derivatives with a combination of 1,3,4-thiadiazole and azine cycles in the molecules and the study of their pesticidal and growth-regulating properties.

## EXPERIMENTAL

<sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were recorded at 30 °C on Varian Mercury-300 spectrometer with standard pulse sequences operating in the mixture of solvents DMSO-*d*<sub>6</sub> and CCl<sub>4</sub> (1:3) using tetra methylsilane (0.0 ppm) as internal standard. The NMR multiplicities brs, s, d, t, q, and m stand for broad singlet, singlet, doublet, triplet, quartet and multiplet, respectively. The reaction progress and purity of the obtained substances were checked by using the tlc method on "Silufol UV-254" plates and acetone/hexane mixture (2:1) as eluent. All melting points were determined in open capillaries and are uncorrected.

**General procedure for the synthesis of compounds 2a-k:**

To a suspension of 0.01 mol of KOH in 7-8 mL of water, 0.01 mol of 5-(alkylthio)-1,3,4-thiadiazole-2(3*H*)-thione was added and then at cooling with glacial water 0.01 mol of 2,4-dichloro-6-alkyl(dialkyl)amino-1,3,5-triazine. The mixture was stirred at room temperature for 1 h, then for 5-6 h at 50-60 °C. The solvent was evaporated, a residue was processed with water and the precipitate was filtered off and purified with benzene.

**2-Chloro-4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazine(2a):**

Flesh-colored crystals; mp 138-139 °C(hexane); yield 85% . <sup>1</sup>HNMR: 2.82 (s, 3H, SCH<sub>3</sub>), 3.20 and 3.22 [ss, 6H, N(CH<sub>3</sub>)<sub>2</sub>]. Anal. Calcd. For C<sub>8</sub>H<sub>9</sub>ClN<sub>6</sub>S<sub>3</sub>: C 29.95, H 2.83, Cl 11.05, N 26.20, S 29.98 %. Found: C 29.99, H 2.90, Cl 10.87, N 26.08, S 30.22 %.

**2-Chloro-4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(methylamino)-1,3,5-triazine(2b):**

Flesh-colored crystals; mp.168-170 °C; yield 70% , <sup>1</sup>HNMR: 2.85 (s, 3H, SCH<sub>3</sub>), 2.90 (d, J=5.2, 3H, NCH<sub>3</sub>), 8.65 (q, J=5.2, 1H, NH). Anal. Calcd. for C<sub>7</sub>H<sub>7</sub>ClN<sub>6</sub>S<sub>3</sub>: C 27.40, H 2.30, Cl 11.55, N 26.39, S 31.35%. Found: C 27.99, H 2.50, Cl 11.58, N 27.40, S 31.42%.

**2-Chloro-4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(ethylamino)-1,3,5-triazine (2c):** Flesh-colored crystals; mp.110-112 °C (benzene); yield 87% , <sup>1</sup>HNMR: 1.20 (t, J=7.1, NCH<sub>2</sub>CH<sub>3</sub>), 2.82 (s, 3H, SCH<sub>3</sub>), 3.38 (m, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 8.65 (t, J=5.3, NH). Anal. Calcd. for C<sub>8</sub>H<sub>9</sub>ClN<sub>6</sub>S<sub>3</sub>: C 29.95, H 2.83, Cl 11.05, N 26.20, S 29.98 %. Found: C 29.99, H 2.90, Cl 11.07, N 26.20, S 30.02 %.

**2-Chloro-4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-(6-isobutylamino)-1,3,5-triazine(2d):**

Flesh-colored crystals; mp.110-112 °C ; yield 85% , <sup>1</sup>HNMR: 0.95 and 0.98 [tt, 6H, J=6.8, (CH<sub>3</sub>)<sub>2</sub>], 1.86 (m, 1H, CH), 2.82 (s, 3H, SCH<sub>3</sub>), 3.10 and 3.15 (m.m, 2H, NCH<sub>2</sub>), 8.77 and 9.00 (tt, J=5.1, NH). Anal. Calcd. for C<sub>10</sub>H<sub>13</sub>ClN<sub>6</sub>S<sub>3</sub>: C 34.43, H 3.76, Cl 10.16, N 24.09, S 27.57%. Found: C 34.55, H 3.80, Cl 10.18, N 24.10, S 27.58%.

**2-Chloro-4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazine(2e):**

Flesh-colored crystals; mp.83-84 °C; yield 80%, <sup>1</sup>HNMR: 1.50 (t, J=7.2, 3H, SCH<sub>2</sub>CH<sub>3</sub>), 3.20 and 3.22 [ss, 6H, N(CH<sub>3</sub>)<sub>2</sub>], 3.38 (q, J=7.2, SCH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd. for C<sub>9</sub>H<sub>11</sub>ClN<sub>6</sub>S<sub>3</sub>: C 32.28, H 3.31, Cl 10.59, N 25.10, S 28.72%. Found: C 32.29, H 3.33, Cl 9.71, N 25.11, S 27.99%.

**2-Chloro-4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(methylamino)-1,3,5-triazine(2f):**

Flesh-colored crystals; mp.143-145 °C ; yield 68% , <sup>1</sup>HNMR: 1.50 (t, J=7.3, 3H, SCH<sub>2</sub>CH<sub>3</sub>), 2.90 (d, J=5.2, NCH<sub>3</sub>), 3.37 (q, J=7.3, SCH<sub>2</sub>CH<sub>3</sub>), 8.42 and 8.68 (brs, 1H, NH). Anal. Calcd. for C<sub>8</sub>H<sub>9</sub>ClN<sub>6</sub>S<sub>3</sub>: C 29.95, H 2.83, Cl 11.05, N 26.20, S 29.98%. Found: C 28.96, H 2.80, Cl 11.03, N 26.10, S 29.58%.

**2-Chloro-4-((5-(propylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazine(2g):**

Flesh-colored crystals; mp.148-150 °C ; yield 77% , <sup>1</sup>HNMR: 1.10 (t, J=7.0, CH<sub>3</sub>-prop.), 1.85 (m, 2H, CH<sub>2</sub>), 3.20 and 3.22 [ss, 6H, N(CH<sub>3</sub>)<sub>2</sub>], 3.35 (t, J=7.2, SCH<sub>2</sub>). Anal. Calcd. for C<sub>10</sub>H<sub>13</sub>ClN<sub>6</sub>S<sub>3</sub>: C 4.43, H 3.76, Cl 10.16, N 24.09, S 27.57%. Found: C 34.56, H 3.80, Cl 10.18, N 24.10, S 27.58%.

**2-Chloro-4-((5-(propylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(diethylamino)-1,3,5-triazine(2h):**

Flesh-colored crystals; mp.96-98 °C; yield 61% , <sup>1</sup>HNMR: 1.10 (t, J=7.1, CH<sub>3</sub>-prop.), 1.13 (t, J=7.0, 6H, NCH<sub>2</sub>CH<sub>3</sub>), 1.85 (m, 2H, CH<sub>2</sub>), 3.36 (t, J=7.1, 2H, SCH<sub>2</sub>), 3.56 (q, J=7.0, 4H, NCH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd. for C<sub>12</sub>H<sub>17</sub>ClN<sub>6</sub>S<sub>3</sub>: C 38.24; H 4.55, Cl 9.40, N 22.30, S 25.52%. Found: C 38.96, H 4.60, Cl 9.43, N 22.31, S 25.54%.

**2-Chloro-4-((5-(isopropylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazine(2i):**

Flesh-colored crystals; mp.78-80 °C; yield 70%, <sup>1</sup>HNMR: 1.50 [d, J=6.7, 6H, (CH<sub>3</sub>)<sub>2</sub>], 3.19 and 3.22

[ss, 6H, N(CH<sub>3</sub>)<sub>2</sub>], 4.05 (m, 1H, SCH). Anal. Calcd. for C<sub>10</sub>H<sub>13</sub>ClN<sub>6</sub>S<sub>3</sub>: C 34.43, H 3.76, Cl 10.16, N 24.09, S 27.57%. Found: C 33.96, H 3.60, Cl 9.75, N 23.85, S 26.54%.

**2-Chloro-4-((5-(isopropylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(diethylamino)-1,3,5-triazine(2j):**

Flesh-colored crystals; mp. 52-54 °C; yield 65%, <sup>1</sup>HNMR: 1.18 and 1.22 (tt, J=7.1, 6H, NCH<sub>2</sub>CH<sub>3</sub>), 1.50 [d, J=6.7, 6H, (CH<sub>3</sub>)<sub>2</sub>], 3.57 and 3.60 (qq, J=7.1, 4H, NCH<sub>2</sub>CH<sub>3</sub>), 4.04 (m, 1H, SCH). Anal. Calcd. for C<sub>10</sub>H<sub>13</sub>ClN<sub>6</sub>S<sub>3</sub>: C 38.24, H 4.55, Cl 9.40, N 22.30, S 25.52%. Found: C 38.56, H 4.60, Cl 9.43, N 22.31, S 25.54%.

**2-Chloro-4-((5-(butylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazine(2k):**

Flesh-colored crystals; mp. 80-82 °C; yield 88%. <sup>1</sup>HNMR: 0.99 (t, J=6.8, CH<sub>3</sub>-but.), 1.50 and 1.78 (mm, 4H, CH<sub>2</sub>CH<sub>2</sub>), 3.20 and 3.22 [ss, 6H, N(CH<sub>3</sub>)<sub>2</sub>], 3.37 (t, J=6.9, 2H, SCH<sub>2</sub>). Anal. Calcd. for C<sub>11</sub>H<sub>15</sub>ClN<sub>6</sub>S<sub>3</sub>: C 36.41, H 4.17, Cl 9.77, N 23.16, S 26.50%. Found: C 36.45, H 4.22, Cl 9.50, N 22.89, S 26.29%.

**2-chloro-4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-methyl-pyrimidine(2l):**

To a suspension of KOH (0.005 mol) in 8-10 mL of DMF, 0.005 mol of (5-ethylthio)-1,3,4-thiadiazole-2(3H)-thione was added, then at cooling with glacial water and continuous stirring, 0.005 mol of 2,4-dichloro-6-methylpyrimidine was added by portions. The mixture was stirred at room temperature for 1-2 h, then at 50-60 °C for 5-6 h. After solvent evaporation the residue was consecutively processed with hexane and NaOH diluted solution. The precipitate was filtered off, washed with water and dried. Yellow crystals; mp. 113-114 °C; yield 85.5%, <sup>1</sup>HNMR: 1.51 (t, J=7.3, SCH<sub>2</sub>CH<sub>3</sub>), 2.49 (s, 3H, CH<sub>3</sub>), 3.39 (q, J=7.3, 2H, SCH<sub>2</sub>CH<sub>3</sub>), 7.46 (s, 1H, CH). Anal. Calcd for C<sub>9</sub>H<sub>9</sub>ClN<sub>4</sub>S<sub>3</sub>: C 35.46, H 2.98, Cl 11.63, S 31.55%. Found: C 35.56, H 3.03, Cl 11.83, N 18.41, S 31.37%.

**(6-Methyl-4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)pyrimidin-2-yl)-trimethyl-ammonium chloride(3):**

To a mixture of 2-chloro-4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-methyl-pyrimidine (2l) (0.0025 mol) in 3 mL of absolute benzene, a solution of triethylamine (0.003 mol) in 5 mL of absolute benzene was added. The mixture was allowed to stand at room temperature for 2 days. The precipitate was filtered off, washed with benzene. Yellow crystals; mp. 208-210 °C; yield 91%. <sup>1</sup>HNMR: 2.52 (s, 3H, CH<sub>3</sub>), 2.82 (s, 3H, SCH<sub>3</sub>), 7.56 (s, 1H, CH). Anal. Calcd for C<sub>12</sub>H<sub>18</sub>ClN<sub>5</sub>S<sub>3</sub>: C 39.60, H 4.99, Cl 9.74, N 19.24, S 26.43%. Found: C 39.72, H 4.88, Cl 9.58, N 19.03, S 26.22%.

**2-(4-methoxycarbonyl-phenoxy)-4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-methyl-pyrimidin (4):**

To a suspension of KOH (0.0016 mol) in 5-7 mL of dry acetone, 0.0016 mol of methyl 4-hydroxybenzoate was added. The mixture was stirred for 1 h, then at cooling with glacial water 0.0015 mol of compound 3 was added. The mixture was stirred at room temperature for 1h, then at 50-55 °C for 5 h. After solvent evaporation the residue was processed with water, the precipitate was filtered off, consecutively washed with KOH diluted solution and water and dried. White crystals; mp. 208-210 °C; yield 91%. <sup>1</sup>HNMR: 2.46 (s, 3H, CH<sub>3</sub>), 2.72 (s, 3H, SCH<sub>3</sub>), 3.91 (s, 3H, OCH<sub>3</sub>), 7.19 (s, 1H, CH), 7.20 and 8.05 (mm, 4H, C<sub>6</sub>H<sub>4</sub>). Anal. Calc. for C<sub>16</sub>H<sub>14</sub> N<sub>4</sub>O<sub>3</sub>S<sub>3</sub>: C 47.28, H 3.47, N 13.78, S 23.66%. Found: C 47.16, H 3.35, N 13.52, S 23.41%.

**General procedure for the synthesis of compounds 5a-c:**

To a solution of thiourea (0.0056 mol) in 10 mL of acetone, 0.005 mol of compound 2 and 1-2 drops of HCl were added. The mixture was heated at 50-60 °C for 4-5 h, acetone was evaporated. To a

residue, 10 mL of water and 0.0011 mol of NaOH were added, and the mixture was heated at 45-50 °C for 1-1.5 h. After cooling and filtration the solution was acidified with HCl to pH 5, and obtained solid was filtered off and washed with water. To purify compounds **5a-c** they were dissolved in a calculated amount of KOH and then acidified with acetic acid.

**4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazine-2-thiol(5a):**

White crystals; mp. 159-160 °C; yield 86%. <sup>1</sup>HNMR: 2.81 (s, 3H, SCH<sub>3</sub>), 3.20 [s, 6H, N(CH<sub>3</sub>)<sub>2</sub>], 14.20 (brs, 1H, SH). Anal. Calc. for C<sub>8</sub>H<sub>10</sub>N<sub>6</sub>S<sub>4</sub>: C 30.17, H 3.17, N 26.39, S 40.27%. Found: C 30.25, H 3.23, N 26.19, S 40.03%.

**4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazine-2-thiol(5b):**

White crystals; mp. 132-133 °C; yield 68%. <sup>1</sup>HNMR: 1.43 (t, J=7.2, 3H, SCH<sub>2</sub>CH<sub>3</sub>), 3.25 (q, J=7.2, SCH<sub>2</sub>CH<sub>3</sub>), 14.25 (brs, 1H, SH). Anal. Calc. for C<sub>9</sub>H<sub>12</sub>N<sub>6</sub>S<sub>4</sub>: C 32.51, H 3.64, N 25.28, S 38.57%. Found: C 32.40, H 3.56, N 25.02, S 38.33%.

**4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-methyl-pyrimidine-2-thiol(5c):**

White crystals; mp. 160-162 °C; yield 73%. <sup>1</sup>HNMR: 1.47 (t, J=7.3, SCH<sub>2</sub>CH<sub>3</sub>), 2.45 (s, 3H, CH<sub>3</sub>), 3.20 (q, J=7.3, 2H, SCH<sub>2</sub>CH<sub>3</sub>), 6.43 (s, 1H, CH), 14.23 (brs, 1H, SH). Anal. Calc. for C<sub>9</sub>H<sub>10</sub>N<sub>4</sub>S<sub>4</sub>: C 35.74, H 3.33, N 18.52, S 42.40%. Found: C 35.81, H 3.22, N 18.26, S 42.22%.

**General procedure for the synthesis of compounds 6a-d:**

In a solution of KOH (0.002 mol) in 4-5 mL of water, 0.002 mol of compound **5** was dissolved. After cooling with glacial water, 0.002 mol of DMS was added, the mixture was stirred for 1-2 h and allowed to stand at room temperature for 10-12 h. To a mixture, 6-8 mL of cool water was added, and compounds **6** were filtered off.

**2-(Methylthio)-4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazine (6a):**

White crystals; mp 138-140 °C; yield 75% , <sup>1</sup>HNMR: 2.44 (s, 3H, 2-SCH<sub>3</sub>), 2.76 (s, 3H, 5-SCH<sub>3</sub>), 3.20 [s, 6H, N(CH<sub>3</sub>)<sub>2</sub>]. Anal. Calcd for C<sub>9</sub>H<sub>12</sub>N<sub>6</sub>S<sub>4</sub>: C 32.51, H 3.64, N 25.28, S 38.57%. Found: C 32.55, H 6.70, N 25.35, S 38.62%.

**2-(Methylthio)-4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazine (6b):**

White crystals; mp 102-103 °C; yield 65% , <sup>1</sup>HNMR: 1.43 (t, J=7.3, SCH<sub>2</sub>CH<sub>3</sub>), 2.44 (s, 3H, 2-SCH<sub>3</sub>), 3.20 [s, 6H, N(CH<sub>3</sub>)<sub>2</sub>], 3.30 (q, J=7.3, 2H, SCH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>10</sub>H<sub>14</sub>N<sub>6</sub>S<sub>4</sub>: C 34.66, H 4.07, N 24.25, S 37.01%. Found: C 34.70, H 4.15, N 25.05, S 37.42%.

**2-((4-((5-(Methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazin-4-yl)thio)acetamide (6c):**

Prepared analogously to the compounds **6a,b** from **5a** and thiourea in the presence of an equimolar amount of NaI. White crystals; mp 150-152 °C; yield 75% , <sup>1</sup>HNMR: 2.78 (s, 3H, SCH<sub>3</sub>), 2.92 [s, 6H, N(CH<sub>3</sub>)<sub>2</sub>], 3.72 and 3.92 (ss, 2H, SCH<sub>2</sub>CO), 7.0 and 7.20 (brs, 2H, NH<sub>2</sub>). Anal. Calcd for C<sub>10</sub>H<sub>13</sub>N<sub>7</sub>OS<sub>4</sub>: C 31.99, H 3.49, N 26.11, S 34.15 Found: C 32.03, H 3.55, N 26.15, S 34.22,

**2-(Methylthio)-4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-methyl-pyrimidine(6d):**

White crystals; mp 130-132 °C; yield 65% , <sup>1</sup>HNMR: 1.43 (t, J=7.3, SCH<sub>2</sub>CH<sub>3</sub>), 2.45 (s, 3H, 2-SCH<sub>3</sub>), 2.47 (s, 3H, CH<sub>3</sub>-pyrim.), 3.35 (q, J=7.3, 2H, SCH<sub>2</sub>CH<sub>3</sub>), 7.44 (s, 1H, CH). Anal. Calcd for C<sub>10</sub>H<sub>12</sub>N<sub>4</sub>S<sub>4</sub>: C 37.95, H 3.82, N 17.70, S 40.52%. Found: C 38.03, H 4.15, N 18.05, S 40.62%.



**General procedure for the synthesis of compounds 7a-d:**

To 0.005 mol of compound **2**, 4 mL of dioxane and 1.2 mL of hydrazine hydrate (70%) were added. The mixture was stirred for 1-2 h and allowed to stand at room temperature for 10-12 h. To a reaction mixture, 5-6 mL of cool water was added, obtained precipitate was filtered off and washed with water.

**2-Hydrazinyl-4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazine (7a).**

White crystals; mp 196-198 °C; yield 89%, <sup>1</sup>HNMR (60 °C): 2.81 (s, 3H, SCH<sub>3</sub>), 3.10 and 3.21 [ss, 6H, N(CH<sub>3</sub>)<sub>2</sub>], 4.23 (brs, 2H, NH<sub>2</sub>), 8.40 (brs, 1H, NH). Anal. Calcd for C<sub>8</sub>H<sub>12</sub>N<sub>8</sub>S<sub>3</sub>: C 30.37, H 3.82, N 35.41, S 30.40 %. Found: C 31.43, H 3.85, N 35.45, S 30.47 %.

**2-Hydrazinyl-4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazine(7b).**

White crystals; mp 149-151 °C; yield 90%, <sup>1</sup>HNMR: 1.48 (t, J=7.0, 3H, SCH<sub>2</sub>CH<sub>3</sub>), 3.10 and 3.22 [ss, 6H, N(CH<sub>3</sub>)<sub>2</sub>], 3.36 (q, J=7.0, SCH<sub>2</sub>CH<sub>3</sub>), 4.20 (brs, 2H, NH<sub>2</sub>), 8.50 (brs, 1H, NH). Anal. Calcd for C<sub>9</sub>H<sub>14</sub>N<sub>8</sub>S<sub>3</sub>: C 32.71, H 4.27, N 33.91, S 29.11 %. Found: C 32.73, H 4.35, N 34.05, S 29.17 %.

**2-Hydrazinyl-4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(ethylamino)-1,3,5-triazine(7c).**

White crystals; mp 190-192 °C; yield 83%, <sup>1</sup>HNMR: 1.18 (t, J=7.1, NCH<sub>2</sub>CH<sub>3</sub>), 2.80 (s, 3H, SCH<sub>3</sub>), 3.37 (m, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 4.30 (brs, 2H, NH<sub>2</sub>), 7.38 and 7.52 (brs, 1H, NHCH<sub>3</sub>), 8.25, 8.42 and 8.60 (brs, 1H, NHNH<sub>2</sub>). Anal. Calcd for C<sub>8</sub>H<sub>12</sub>N<sub>8</sub>S<sub>3</sub>: C 30.37, H 3.82, N 35.41, S 30.40 %. Found: C 30.73, H 3.90, N 35.45, S 30.47 %.

**2-Hydrazinyl-4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-methyl-pyrimidine(7d).**

White crystals; mp 151-152 °C; yield 78%, <sup>1</sup>HNMR: 1.48 (t, J=7.1, 3H, SCH<sub>2</sub>CH<sub>3</sub>), 2.30 (s, 3H, CH<sub>3</sub>-pyrim.), 3.35 (q, J=7.1, SCH<sub>2</sub>CH<sub>3</sub>), 4.18 (brs, 2H, NH<sub>2</sub>), 6.48 (s, 1H, CH-pyrim), 8.23 (brs, 1H, NH). Anal. Calcd for C<sub>9</sub>H<sub>12</sub>N<sub>6</sub>S<sub>3</sub>: C 35.98, H 4.03, N 27.98, S 32.02 %. Found: C 36.03, H 4.10, N 28.05, S 32.07 %.

**General procedure for the synthesis of compounds 8a-d:**

To a suspension of 0.002 mol of compound **7** in 2 mL of acetic acid and 1.5 mL of pentane-2,4-dione, 1-2 drops of DMF was added. The mixture was stirred and allowed to stand at room temperature for 12-14 h. After adding of cool water (5-6 mL) the obtained presipitate was filtered off, washed with diluted solution of HCl, then water and dried.

**2-(3,5-dimethyl-1H-pyrazol-1-yl)-4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazine (8a):**

White crystals; mp 208-210 °C; yield 78% (benzene), <sup>1</sup>HNMR: 2.80 (s, 3H, SCH<sub>3</sub>), 2.24 (s, 3H, 3-CH<sub>3</sub>-pyraz.), 2.56 (s, 3H, 5-CH<sub>3</sub>-pyraz.), 3.22 and 3.24 [ss, 6H, N(CH<sub>3</sub>)<sub>2</sub>], 6.00 (s, 1H, CH-pyraz.). Anal. Calcd for C<sub>13</sub>H<sub>16</sub>N<sub>8</sub>S<sub>3</sub>: C 41.04, H 4.24, N 29.45, S 25.28 %. Found: C 41.03, H 4.15, N 29.25, S 25.17 %.

**2-(3,5-dimethyl-1H-pyrazol-1-yl)-4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(ethylamino)-1,3,5-triazine (8b):**

White crystals; mp 172-173 °C; yield 66% (ethanol), <sup>1</sup>HNMR: 1.51 (t, J=7.1, 3H, SCH<sub>2</sub>CH<sub>3</sub>), 2.26 (s, 3H, 3-CH<sub>3</sub>-pyraz.), 2.58 (s, 3H, 5-CH<sub>3</sub>-pyraz.), 3.25 and 3.27 [ss, 6H, N(CH<sub>3</sub>)<sub>2</sub>], 3.36 (q, J=7.1, SCH<sub>2</sub>CH<sub>3</sub>), 6.02 (s, 1H, CH-pyraz.). Anal. Calcd for C<sub>13</sub>H<sub>16</sub>N<sub>8</sub>S<sub>3</sub>: C 41.04, H 4.24, N 29.45, S 25.28 %. Found: C 41.07, H 4.25, N 29.55, S 25.37 %.

**2-(3,5-dimethyl-1H-pyrazol-1-yl)-4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazine (8c):**

White crystals; mp 168-169 °C; yield 70% (ethanol) , <sup>1</sup>HNMR: 1.21 and 1.23 (t,t, J=7.0, 3H, NCH<sub>2</sub>CH<sub>3</sub>), 2.20 and 2.26 (s, 3H, 3-CH<sub>3</sub>-pyraz.), 2.48 and 2.60 (s, 3H, 5-CH<sub>3</sub>-pyraz.), 2.81 (s, 3H, SCH<sub>3</sub>), 3.37-3.49 (mm, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 5.97 and 6.01 (s, 1H, CH-pyraz.), 8.40 and 8.69 (t, J=5.6, 1H, NH). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>8</sub>S<sub>3</sub>: C 42.62, H 4.60, N 28.40, S 24.38 %. Found: C 42.67, H 4.65, N 28.55, S 24.47 %.

**2-(3,5-Dimethyl-1H-pyrazol-1-yl)-4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-methyl-pyrimidine (8d):**

White crystals; mp 109-110 °C; yield 83% (benzene) , <sup>1</sup>HNMR: 1.51 (t, J=7.1, 3H, SCH<sub>2</sub>CH<sub>3</sub>), 2.25 (s, 3H, 3-CH<sub>3</sub>-pyraz.), 2.50 and 2.52 (ss, 6H, CH<sub>3</sub>-pyrim. and 5-CH<sub>3</sub>-pyraz.), 3.36 (q, J=7.1, SCH<sub>2</sub>CH<sub>3</sub>), 5.96 (s, 1H, CH-pyraz.), 7.22 (s, 1H, CH-pyrim.). Anal. Calcd for C<sub>14</sub>H<sub>16</sub>N<sub>6</sub>S<sub>3</sub>: C 46.13, H 4.42, N 23.06, S 26.39 %. Found: C 46.27, H 4.55, N 23.11, S 26.47 %.

**General procedure for the synthesis of compounds 9a-d:**

To a mixture of compound **7** (0.002 mol) in 1 mL of glacial acetic acid, 2 mL of 3-oxobutanoate and 1-2 drops of DMF were added. The mixture was allowed to stand at room temperature for 20-22 h. After adding of cool water (6-8 mL) the obtained precipitate was filtered off and consecutively washed with diluted HCl, water and dried.

**Ethyl3-(2-(4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazin-2-yl)hydrazono)butanoate (9a):**

White crystals; mp 83-84 °C; yield 90%. <sup>1</sup>HNMR: 1.24 (t, J=7.1, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 1.88 and 2.00 (ss, 3H, CCH<sub>3</sub>), 2.80 (s, 3H, SCH<sub>3</sub>), 3.15 and 3.20 [ss, 6H, N(CH<sub>3</sub>)<sub>2</sub>], 3.32 and 3.50 (s.s, 2H, COCH<sub>2</sub>), 4.15 (q, J=7.1, OCH<sub>2</sub>CH<sub>3</sub>), 9.60, 9.90 and 10.04 (brs, 1H, NH). Anal. Calcd for C<sub>14</sub>H<sub>20</sub>N<sub>8</sub>O<sub>2</sub>S<sub>3</sub>: C 39.24, H 4.70, N 26.15, S 22.44 %. Found: C 39.08, H 4.59, N 25.84, S 22.20 %.

**Ethyl3-(2-(4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(dimethylamino)-1,3,5-triazin-2-yl)hydrazono)butanoate (9b):**

White crystals; mp 138-140 °C; yield 75%(ethanol), <sup>1</sup>HNMR: 1.28 (t, J=7.1, OCH<sub>2</sub>CH<sub>3</sub>), 1.48 (t, J=7.3, 3H, SCH<sub>2</sub>CH<sub>3</sub>), 1.88 and 2.02 (ss, 3H, CCH<sub>3</sub>), 3.10-3.40 [m, 10H, N(CH<sub>3</sub>)<sub>2</sub>, COCH<sub>2</sub>, SCH<sub>2</sub>CH<sub>3</sub>], 4.14 (q, J=7.1, OCH<sub>2</sub>CH<sub>3</sub>), 9.60 and 9.87 (brs, 1H, NH). Anal. Calcd for C<sub>15</sub>H<sub>22</sub>N<sub>8</sub>O<sub>2</sub>S<sub>3</sub>: C 40.71, H 5.01, N 25.32, S 21.73 %. Found: C 40.55, H 4.88, N 25.08, S 21.56 %.

**Ethyl3-(2-(4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(ethylamino)-1,3,5-triazin-2-yl)hydrazono) butanoate (9c):**

White crystals; mp 96-98 °C; yield 70%(ethanol) , <sup>1</sup>HNMR: 1.20 (t, J=7.1, OCH<sub>2</sub>CH<sub>3</sub>), 1.22 and 1.24 (t, J=7.0, 3H, NCH<sub>2</sub>CH<sub>3</sub>), 1.88 and 2.02 (ss, 3H, CCH<sub>3</sub>), 2.80 (s, 3H, SCH<sub>3</sub>), 3.32-3.45 (m, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 3.25 and 3.38 (ss, 2H, COCH<sub>2</sub>), 4.14 (q, J=7.1, OCH<sub>2</sub>CH<sub>3</sub>), 7.60 and 7.72 (brs, 1H, NHCH<sub>3</sub>), 9.80 and 9.90 (brs, 1H, NH). Anal. Calcd for C<sub>14</sub>H<sub>20</sub>N<sub>8</sub>O<sub>2</sub>S<sub>3</sub>: C 39.24, H 4.70, N 26.15, S 22.44 %. Found: C 39.10, H 4.53, N 25.90, S 22.22 %.

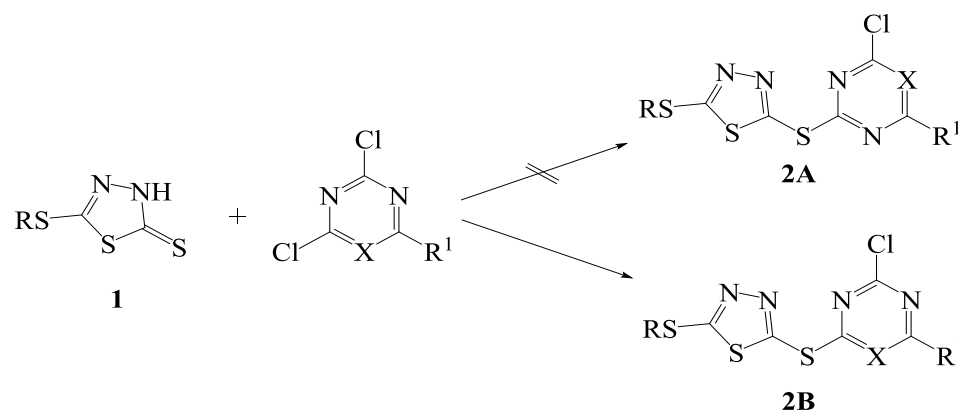
**Ethyl3-(2-(4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-methyl-pyrimidin-2-yl)hydrazono) butanoate (9d):**

White crystals; mp 109-110 °C; yield 74% , <sup>1</sup>HNMR: 1.29 (t, J=7.1, OCH<sub>2</sub>CH<sub>3</sub>), 1.47 (t, J=7.3, 3H, SCH<sub>2</sub>CH<sub>3</sub>), 1.80 and 2.05 (ss, 3H, CCH<sub>3</sub>), 2.34 and 2.35 (s, 3H, CH<sub>3</sub>-pyrim.), 3.33 (q, J=7.3, 2H, SCH<sub>2</sub>CH<sub>3</sub>), 3.37 and 3.50 (ss, 2H, COCH<sub>2</sub>), 4.14 (q, J=7.1, OCH<sub>2</sub>CH<sub>3</sub>), 6.69 and 6.71 (ss, 1H, CH-

pyrim.), 9.69 and 9.94 (brs, 1H, NH). Anal. Calcd for  $C_{15}H_{20}N_6O_2S_3$ : C 43.67, H 4.89, N 20.37, S 23.31 %. Found: C 43.49, H 4.78, N 20.12, S 23.14 %.

## RESULTS AND DISCUSSION

In our early studies we have synthesized mono-, di- and bis-alkylthio derivatives of 1,3,4-thiadiazolidine-2,5-dithione<sup>10,11</sup>. Considering the detected pesticidal activity of some compounds of these series, as well as the availability and high yield obtainment of starting 1,3,4-thiadiazol-2,5-dithione it was advisable to conduct a number of syntheses based on this compound. The treatment of 5-(alkylthio)-1,3,4-thiadiazole-2(3*H*)-thione (**1**) with 2,4-dichloro-6-alkyl(dialkyl)amino-1,3,5-triazines and 2,4-dichloro-6-methyl-pyrimidine leads to 2-chloro-4-((5-(alkylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(alkyl(dialkyl)amino)-1,3,5-triazines (**2**, X=N) and 2-chloro-4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)-6-methyl-pyrimidine (**2**, X=CH).



**2a-k** X=N; **2a-d** R = CH<sub>3</sub>, **2e,f** R = C<sub>2</sub>H<sub>5</sub>, **2g,h** R = n-C<sub>3</sub>H<sub>7</sub>,

**2i,j** R = i-C<sub>3</sub>H<sub>7</sub>, **2k** R = n-C<sub>4</sub>H<sub>9</sub>, **2l** X=CH; R = C<sub>2</sub>H<sub>5</sub>, R<sub>1</sub> = CH<sub>3</sub>

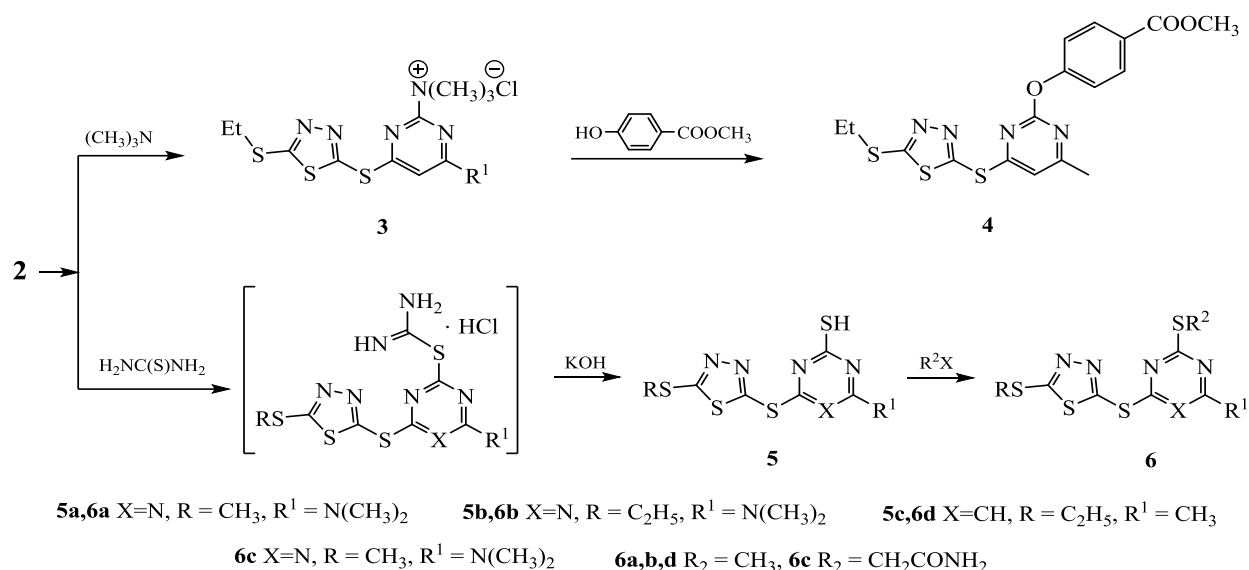
**Scheme 1:** Synthesis of 2-chloro-4-((5-(alkylthio)-1,3,4-thiadiazol-2-yl)thio)-azines

A substitution of any one chlorine atom in triazine ring leads to the same product, because this cycle is symmetrical. However, the pyrimidine cycle is asymmetric and it is necessary to establish the position of substitution in this ring. The choice between the two possible structures (**2A** and **2B**) was done on the base of <sup>13</sup>C NMR spectra, taking into account the influence of substituents on the chemical shifts of pyrimidine carbon atoms.

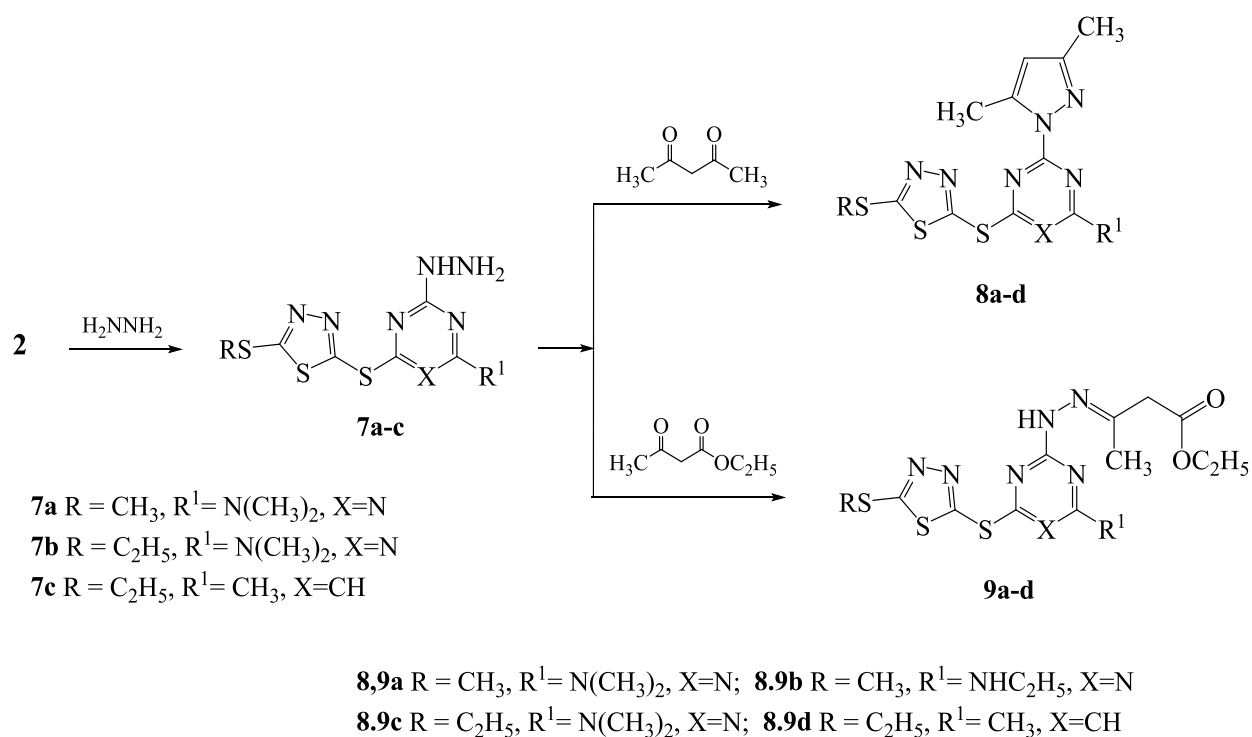
It is known that by replacing the chlorine atom on S-alkyl or S-phenyl radical the chemical shift of the attached carbon atom of the heterocycle (C-2 or C-4) should be shifted downfield by 4 ppm. The signal of C-4, which accurately identified in coupled <sup>13</sup>C NMR spectra recorded without suppression of <sup>13</sup>C–<sup>1</sup>H spin-spin interaction, observed as a doublet due to spin-spin interaction with the hydrogen atom at C-5 (<sup>2</sup>J = 2.1 Hz). In <sup>13</sup>C NMR spectra of compound **2l** the signal of this carbon atom is shifted downfield by 6 ppm, compared to the starting compound, which is consistent with substitution of the chlorine atom of the 4th position of pyrimidine ring (**2B**).

Compound **2l** with trimethylamine forms corresponding (6-methyl-4-((5-(ethylthio)-1,3,4-thiadiazol-2-yl)thio)pyrimidin-2-yl)-trimethyl-ammonium chloride (**3**). The reaction of this salt with methyl 4-hydroxybenzoate afforded 2-(4-methoxycarbonyl-phenoxy)-4-((5-(methylthio)-1,3,4-thiadiazol-2-yl)thio)-6-methyl-pyrimidine (**4**).





**Scheme 2:** Synthesis of 2-O or 2-S-substituted 4-((5-(alkylthio)-1,3,4-thiadiazol-2-yl)thio)-azines



**Scheme 3:** Synthesis and transformations of 2-hydrazinyl-4-((5-(alkylthio)-1,3,4-thiadiazol-2-yl)thio)-azines

The interaction of 2-chloro-4-((5-(alkylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(alkyl(dialkyl)amino)-1,3,5-triazines with thiourea in the presence of catalytic amounts of HCl and further decomposition of intermediate 4-((5-(alkylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(alkyl(dialkyl)amino)-1,3,5-triazin-2-yl carbamimidothioate hydrochlorides with KOH in the reaction mixture leads to 4-((5-(alkylthio)-1,3,4-thiadiazol-2-yl)thio)-6-(alkyl(dialkyl)amino)-1,3,5-triazine-2-thiols (**5**). These thiols (**5**) are easily

alkylated, forming the corresponding alkyl derivatives (**6**). The hydrazinolysis of some compounds **2** with hydrazine hydrate water solution occurs very easy at room temperature in 12-16 h, and corresponding 2-hydrazinyl substituted derivatives (**7**) are formed. Their cyclization with pentane-2,4-dione afforded 2-(3,5-dimethyl-1*H*-pyrazol-1-yl) substituted derivatives (**8**). At the same time the reaction of 2-hydrazinyl derivatives (**7**) with ethyl 3-oxobutanoate leads to acyclic hydrazono-butanoates (**9**) formation.

## BIOLOGICAL ASSAY

At preliminary screening the herbicidal, fungicidal and growth regulatory activities of novel synthesized compounds were studied. All preparations did not possess noticeable herbicidal or antifungal properties, but they showed the pronounced growth stimulate activity. The object of study were the seeds and seedlings of common bean (*Phaseolus vulgaris* L.). The laboratory experiments were performed on two schemes. By the first scheme the effect of aqueous suspension of compounds **2-9** and heteroauxin (IAA) in concentrations 25 and 50 mg L<sup>-1</sup> on the viability of seeds, germination and seedlings were studied. The seeds were incubated for 24 hours in an appropriate mediums in the dark at 25°C. Then the seeds were transplanted into soil and watered daily. The experiment was repeated twice.

By the second experimental setup the bean seeds were sown in the soil in small vessels. When the length of the stems reached 15-20 cm, plants were dug out, the root parts were washed with water and cut off. Series of 8-10 cut plants were immersed in the prepared aqueous solutions of IAA and investigated preparations in concentrations 25 mg L<sup>-1</sup> and 50 mg L<sup>-1</sup>. After 24 hours, they were washed and dipped into the vessels with water. Water in the vessels was changed every day. The formation of root system has already been observed on 8-9 day. The calculations were produced in 20-25 days. The experiment was repeated twice. The number of the plants roots of each series, their length and weight in the moist and dry forms, their average values were calculated. The obtained results of both experiments for synthesized compounds solutions were compared with similar data of plants placed in IAA solutions, on the basis of which the activities of preparations were determined in comparison with IAA (in %).

All obtained compounds had growth stimulant properties, the activity of 6 compounds were higher than 75%, one of them (**21**) have shown 100% activity. These six preparations are preparing for further field trials.

## CONCLUSIONS

The simple and convenient high yield methods for the synthesis of novel nonfused bi- and triheterocyclic systems derivatives with a combination of 1,3,4-thiadiazole, 1,3,5-triazine, pyrimidine and pyrazole rings in the same molecules were elaborated. The synthesized compounds have shown the pronounced plant growth stimulant properties. Six compounds having high activity (75-100%, compared with heteroauxin) were selected for deeper study and further field trials. These results of the study indicate that the new synthesized heterocyclic systems can be of interest for the search of new plants growth stimulators.

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