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Facile Synthesis of 6-Hetaryl[1,2,4]triazolo[3,4-*b*][1,3,4]-thiadiazoles and 7-Hetaryl[1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazines with Fungicidal Activity*

E. M. El-Telbani, R. H. Swellem, and G. A. M. Nawwar

Pesticides Laboratory, National Research Center, Dokki, Cairo, Egypt

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Abstract—Condensation of 4-amino-4*H*-1,2,4-triazole-3-thiol and 4-amino-6-methyl-3-sulfanyl-1,2,4-triazin-5(4*H*)-one with ethyl cyanoacetate gave ethyl [1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazol-6-ylacetate and ethyl 3-methyl-4-oxo-4*H*-[1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazin-7-ylacetate, respectively. Reactions of the condensation products with 1,3-diphenylprop-2-en-1-one, aromatic aldehydes, and carbon disulfide or *N*,*N*-dimethylformamide dimethyl acetal (followed by treatment with hydrazine hydrate) gave the corresponding 6-hetaryl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazoles and 7-hetaryl-3-methyl-4*H*-[1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazin-4-ones. Preliminary tests revealed fungicidal activity of the pyrazolyl-substituted derivatives.

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Various 1,2,4-triazole derivatives were found to exhibit diverse pharmacological activity [1–4]. The thiadiazole nucleus incorporating a toxophoric N–C–S moiety also gives rise to biological activity [5, 6]. In our previous work, we were interested in the synthesis of 2-heteroaryl-substituted benzazoles [7, 8] due to their fungicidal activity especially in the agrochemical field [9]. Substituting a triazine or a triazole moiety for the difficultly biodegradable benzene ring in 2-heteroarylbenzazoles might result in better biological output [10] or lead to easily degradable and environmentally safe compounds.

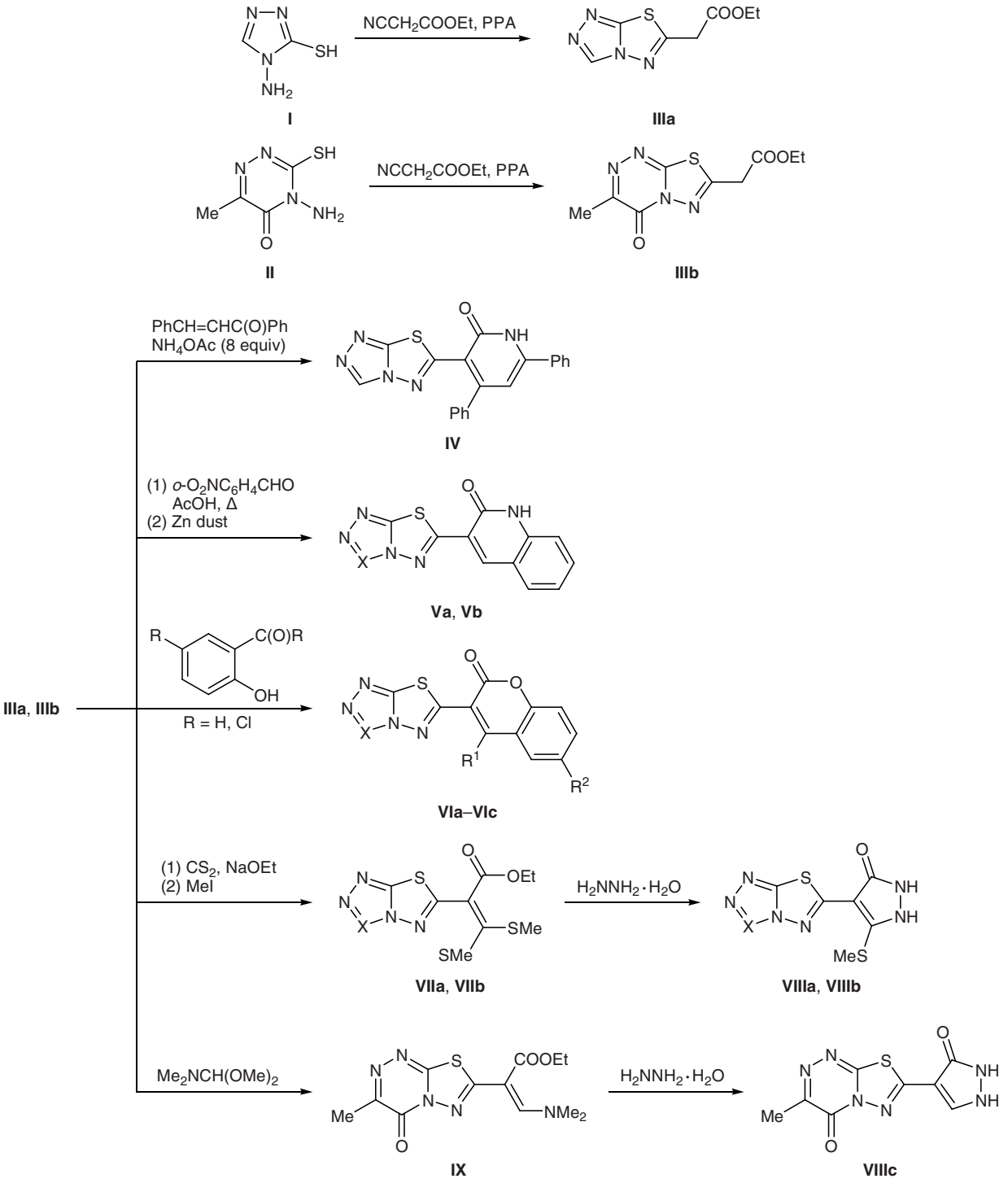
The reaction of 4-amino-4*H*-1,2,4-triazole-3-thiol (**I**) with ethyl cyanoacetate in the presence of polyphosphoric acid at 120°C gave a product which showed in the ^{1}H NMR spectrum a methylene proton singlet at δ 4.1 ppm, signals from the ethyl protons at δ 1.3 (t) and 4.3 ppm (q), and a singlet at δ 8.8 due to CH proton in the triazole ring. Its IR spectrum contained an absorption band at 1720 cm^{-1}, typical of ester carbonyl, and the molecular ion peak was detected at *m*/*z* 212 in the mass spectrum. On the basis of these data, the condensation product was assigned the structure of ethyl [1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazol-6-ylacetate (**IIIa**) (Scheme 1). Triazine-fused analog **IIIb** was obtained under similar conditions by condensation of ethyl cyanoacetate with 4-amino-6-methyl-3-sulfanyl-1,2,4-triazin-5(4*H*)-one (**II**). Presumably, compounds **IIIa** and **IIIb** were formed via nucleophilic addition of amino thiols **I** and **II** at the cyano group of ethyl cyanoacetate, followed by cyclization with elimination of ammonia.

Molecules **IIIa** and **IIIb** possess a chemically active side chain which makes them capable of undergoing further transformations. Acetate **IIIa** was treated with 1,3-diphenylprop-2-en-1-one in presence of 8 equiv of ammonium acetate to obtain pyridin-2-one derivative **IV**. The ^{1}H NMR spectrum of **IV** contained a singlet at δ 6.8 ppm from 5-H in the pyridine ring and a singlet at δ 9.2 ppm from 3-H in the triazolothiadiazole system. In the mass spectrum of **IV**, the molecular ion peak with *m*/*z* 371 was present. In keeping with the data of [12, 13], intermediate tetrahydropyridine derivatives is oxidized during the reaction to give dihydropyridine **IV**.

Compounds **IIIa** and **IIIb** were also brought into reactions with *ortho*-substituted aldehydes. Treatment of **IIIa** with 2-nitrobenzaldehyde in boiling acetic acid, followed by addition of Zn powder, resulted in the formation of 6-(2-oxo-1,2-dihydroquinolin-3-yl)-substituted triazolothiadiazole **Va**. The product structure was determined on the basis of the analytical and spectral data. In the IR spectrum of **Va** we observed a lactam carbonyl band at 1660 cm^{-1}; the 4-H proton resonated at δ 8.7 ppm [14] in the ^{1}H NMR spectrum,

* The text was submitted by the authors in English.

Scheme 1.



V–**VIII**, X = CH (**a**), C(Me)–C(O) (**b**); **VIa**, **VIb**, $R^1 = R^2 = H$; **VIc**, X = CH, R^1 = HO, R^2 = Cl.

and the signal from 3-H in the triazolothiadiazole fragment appeared at δ 9.2 ppm. Likewise, compound **IIIb** reacted with 2-nitrobenzaldehyde under similar reaction conditions to give 7-quinolinyl-substituted thiadiazolotriazine **Vb** which showed in the mass spectrum the molecular ion peak $[M]^+$ at *m*/*z* 311. Products **Va** and **Vb** are likely to be formed via condensation of the aldehyde at the activated methylene group in **IIIa** or **IIIb**, reduction of the nitro group to amino, and subsequent cyclization at the ester moiety with loss of

ethanol. The condensation of salicylaldehyde with methylene-active compounds **IIIa** and **IIIb** was also accompanied by intramolecular cyclization with formation of the corresponding coumarin derivatives **VIa** and **VIb** (Scheme 1). Compounds **VIa** and **VIb** displayed in the ^{1}H NMR spectra a signal at δ 9.2 ppm [15] due to 4-H in the pyran ring, and the lactone carbonyl group gave rise to IR absorption at ~1700 cm^{-1}.

4-Hydroxycoumarin analog **VIc** was obtained in a fairly good yield by reaction of **IIIa** with 5-chlorosalicyloyl chloride. Unlike compounds **VIa** and **VIb**, no coumarin 4-H signal was present in the ^{1}H NMR spectrum of **VIc**, but a broadened singlet (exchangeable with D_2O) appeared at δ 10.3 ppm due to the 4-OH group. The elemental composition and an *m*/*z* value of 320 for the molecular ion peak in the mass spectrum of compound **VIc** were consistent with the assumed structure.

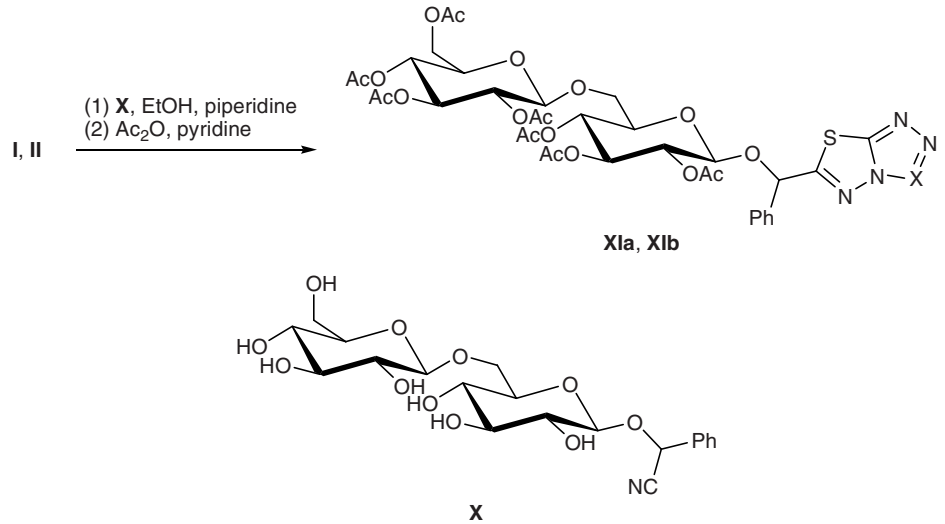
With a view to prepare heteroanalogs of the commercially available fungicides Fuberidazole [16] and Thiabendazole [17], compounds **III** were treated with carbon disulfide in the presence of sodium ethoxide and excess methyl iodide. These reactions afforded the corresponding bis(methylsulfanyl)methylidene derivatives **VIIa** and **VIIb** whose MeS protons resonated at δ 2.6 ppm in the ^{1}H NMR spectra ($CDCl_3$); no signal assignable to active methylene protons, which is typical of parent compounds **III**, was observed. By treatment of compounds **VIIa** and **VIIb** with hydrazine hydrate (80% w/w) we obtained new products which showed no ethoxy group protons in the ^{1}H NMR spectra; a singlet corresponding to one methylsulfanyl group was observed at δ 2.5 ppm, and two new downfield signals (exchangeable with D_2O) appeared at δ 10.5 and 8.5 ppm. In the mass spectrum of **VIIIa**, the molecular ion peak with *m*/*z* 254 was present. These data lead us to assign 2,3-dihydro-1*H*-pyrazol-3-one structure to compounds **VIIIa** and **VIIIb**.

The reaction of **IIIb** with *N*,*N*-dimethylformamide dimethyl acetal gave adduct **IX** in moderate yield. The ylidene proton in **IX** gave rise to a signal at δ 8.2 ppm in the ^{1}H NMR spectrum, and the signal at δ 3.2 ppm was assigned to the dimethylamino group. The mass spectrum of **IX** contained the molecular ion peak at *m*/*z* 309. The carbonyl stretching vibration frequency in the IR spectrum of **IX** was considerably lower than that observed for parent compound **IIIb** as a result of conjugation between the carbonyl group and enamine moiety. The chemical behavior of compound **IX** provided an additional proof for the assumed structure. Treatment of **IX** with hydrazine hydrate (80% w/w) gave pyrazolone **VIIIc** (*m*/*z* ~250 $[M]^+$; $\delta_{5\text{-H}}$ 6.8 ppm). The elemental analysis and IR spectral data were in agreement with structure **VIIIc**.

Finally, compounds **I** and **II** were brought into reaction with Amygdalin (**X**, a cyano glycoside derivative) in the presence of piperidine as catalyst, followed by acylation with a mixture of pyridine and acetic anhydride, to obtain β-anomeric glycoside derivatives **XIa** and **XIb**, respectively (Scheme 2, see Experimental).

Preliminary tests showed that compounds **VIIIa** and **VIIIb** exhibited an appreciable fungicidal activity against *F. manilifarm*, *P. oxalicum*, and *A. niger*.

Scheme 2.



XI, X = CH (**a**), C(Me)–C(O) (**b**).

Further studies on fungicidal activity of the synthesized triazolothiadiazole and thiadiazolotriazine derivatives are now in progress, and their results will be published elsewhere.

EXPERIMENTAL

All melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. The IR spectra were recorded in KBr pellets using a UR 10 (Carl Zeiss) spectrophotometer. The ^{1}H NMR spectra were measured on a Jeol instrument operating at 270 MHz using tetramethylsilane as internal reference. The mass spectra were run on a Finigan SSQ 7000 mass spectrometer. The elemental compositions were determined at the Central Service Laboratory, National Research Centre, and at the Analyses Unit, Cairo University.

Ethyl [1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazol-6-ylacetate (IIIa) and ethyl 3-methyl-4-oxo-4*H*-[1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazin-7-ylacetate (IIIb) (*general procedure*)**.** A mixture of 10 mmol of compound **I** or **II** and 10 mmol of ethyl cyanoacetate in 10 ml of polyphosphoric acid was heated for 1 h at 120°C. The mixture was cooled, diluted with 100 ml of water, made alkaline by adding sodium hydrogen carbonate, and extracted with ethyl acetate (3×10 ml). The extract was dried over anhydrous magnesium sulfate and evaporated to dryness, and the residue was purified by recrystallization.

Compound **IIIa**. Yield 70%, mp 106–108°C (from ethanol). IR spectrum: ν 1720 cm^{-1} (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.3 t (3H, CH_3), 4.1 s (2H, CH_2), 4.3 q (2H, OCH_2), 8.8 s (1H, CH=N). Mass spectrum: *m*/*z* 212 $[M]^+$. Found, %: C 39.5; H 3.5; N 26.6; S 14.9. $C_7H_8N_4O_2S$. Calculated, %: C 39.6; H 3.8; N 26.4; S 15.1%. *M* 212.23.

Compound **IIIb**. Yield 75%, mp 114–116°C (from ethanol). IR spectrum, ν, cm^{-1}: 1715 (C=O, ester), 1693 (CO). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.3 t (3H, $CH_2C\mathbf{H}_3$), 2.6 s (3H, 3-CH_3), 4.1 s (2H, CH_2), 4.3 q (2H, OCH_2). Found, %: C 42.3; H 3.7; N 21.7; S 12.3. $C_9H_{10}N_4O_3S$. Calculated, %: C 42.5; H 3.9; N 22.0; S 12.6.

4,6-Diphenyl-3-([1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazol-6-yl)pyridin-2(1*H*)-one (IV). A mixture of 10 mmol of compound **IIIa**, 10 mmol of 1,3-diphenylprop-2-en-1-one, and 80 mmol of ammonium acetate in 20 ml of ethanol was heated for 12 h under reflux. A solid product separated and was filtered off, washed with water and ethanol, and recrystallized. Yield 68%, mp 309–310°C (from butan-1-ol). IR spectrum, ν, cm^{-1}: 3233 (NH), 1643 (C=O), 1616 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.8 s (1H, 5-H), 7.5–8.0 m (10H, C_6H_5), 9.2 s (1H, CH=N), 13.0 br.s (1H, NH). Mass spectrum: *m*/*z* 371 $[M]^+$. Found, %: C 64.5; H 3.5; N 18.6; S 8.9. $C_{20}H_{13}N_5OS$. Calculated, %: C 64.7; H 3.5; N 18.9; S 8.6. *M* 371.42.

3-([1,2,4]Triazolo[3,4-*b*][1,3,4]thiadiazol-6-yl)-quinolin-2(1*H*)-one (Va) and 3-(3-methyl-4-oxo-4*H*-[1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazin-7-yl)quinolin-2(1*H*)-one (Vb) (*general procedure*)**.** A mixture of 10 mmol of compound **IIIa** or **IIIb** and 10 mmol of 2-nitrobenzaldehyde in 20 ml of acetic acid was heated for 5 h under reflux. Zinc powder, 3 g, was then added in portions, and the mixture was heated under reflux for an additional 4 h. The mixture was filtered, the filtrate was poured into water and made alkaline by adding sodium hydrogen carbonate, and the precipitate was filtered off and recrystallized from appropriate solvent.

Compound **Va**. Yield 50%, mp 251–253°C (from ethanol). IR spectrum, ν, cm^{-1}: 3230 (NH), 1660 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.5–7.7 m (4H, 5-H–8-H, quinoline), 8.7 s (1H, 4-H), 9.2 s (1H, 4′-H), 10.8 s (1H, NH). Found, %: C 53.3; H 2.4; N 25.8; S 11.8. $C_{12}H_7N_5OS$. Calculated, %: C 53.5; H 2.6; N 26.0; S 11.9%.

Compound **Vb**. Yield 65%, mp 248–249°C (from ethanol). IR spectrum, ν, cm^{-1}: 3200 (NH); 1660, 1665 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.3 s (3H, CH_3), 7.6–7.7 m (4H, 5-H–8-H, quinoline), 8.8 s (1H, 4-H), 10.9 s (1H, NH). Mass spectrum: *m*/*z* 311 $[M]^+$. Found, %: C 50.8; H 2.8; N 22.3; S 10.0. $C_{14}H_9N_5O_2S$. Calculated, %: C 51.0; H 2.9; N 22.5; S 10.3. *M* 311.25.

3-([1,2,4]Triazolo[3,4-*b*][1,3,4]thiadiazol-6-yl)-2*H*-chromen-2-one (VIa) and 3-(3-methyl-4-oxo-4*H*-[1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazin-7-yl)-2*H*-chromen-2-one (VIb) (*general procedure*)**.** A mixture of 10 mmol of compound **IIIa** or **IIIb** and 10 mmol of salicylaldehyde in 20 ml of acetic acid was heated for 6–8 h under reflux. It was then concentrated, and the precipitate was filtered off and recrystallized.

Compound **VIa**. Yield 80%, mp 296–298°C (from butan-1-ol). IR spectrum: ν 1700 cm^{-1} (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.4–8.1 m (4H, C_6H_4), 9.2 s (1H, 4-H), 9.7 s (1H, CH=N). Found, %: C 53.2; H 2.2; N 20.6; S 11.7. $C_{12}H_6N_4O_2S$. Calculated, %: C 53.3; H 2.2; N 20.7; S 11.9.

Compound **VIb**. Yield 70%, mp 290–292°C (from butan-1-ol). IR spectrum, ν, cm^{-1}: 1700 (C=O, lactone), 1660 (C=O, lactam). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.7 s (3H, CH_3), 7.6–7.8 m (4H, C_6H_4), 9.4 s (1H, 4-H). Found, %: C 53.9; H 2.5; N 17.7; S 10.0. $C_{14}H_8N_4O_3S$. Calculated, %: C 53.8; H 2.6; N 17.9; S 10.3.

6-Chloro-4-hydroxy-3-([1,2,4]triazolo[3,4-*b*]-[1,3,4]thiadiazol-6-yl)-2*H*-chromen-2-one (VIc). A solution of 10 mmol of 5-chlorosalicyloyl chloride in 5 ml of anhydrous tetrahydrofuran was added dropwise under stirring over a period of 15 min to a solution of 10 mmol of compound **IIIa** and 20 mmol of triethylamine in 20 ml of anhydrous tetrahydrofuran, cooled to 0°C. The mixture was then stirred for 2 h at room temperature, poured into water, and acidified with dilute hydrochloric acid. The precipitate was filtered off, washed with water, and purified by recrystallization. Yield 30%, mp 160–162°C (from acetic acid). IR spectrum, ν, cm^{-1}: 3340 (OH), 1700 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 7.2–7.9 m (3H, 5-H, 7-H, 8-H), 9.8 s (1H, CH=N), 10.3 br.s (1H, OH). Mass spectrum: *m*/*z* 320 $[M]^+$. Found, %: C 44.8; H 1.6; Cl 11.0; N 17.7; S 10.2. $C_{12}H_5ClN_4O_3S$. Calculated, %: C 44.9; H 1.6; Cl 11.1; N 17.5; S 10.0. *M* 320.71.

Ethyl 3,3-bis(methylsulfanyl)-2-([1,2,4]triazolo-[3,4-*b*][1,3,4]thiadiazol-6-yl)acrylate (VIIa) and ethyl 2-(3-methyl-4-oxo-4*H*-[1,3,4]thiadiazolo-[2,3-*c*][1,2,4]triazin-7-yl)-3,3-bis(methylsulfanyl)-acrylate (VIIb) (*general procedure*). A solution of 10 mmol of compound **IIIa** or **IIIb** in 10 ml of ethanol was cooled, and 5 ml of sodium ethoxide, 2 ml of carbon disulfide, 5 ml of sodium ethoxide, and finally 5 ml of carbon disulfide were added in succession at 15-min intervals. After the addition was complete, the mixture was stirred for one hour, and 20 mmol of methyl iodide was added dropwise over a period of 2 h under stirring at room temperature. The mixture was then poured onto crushed ice and acidified with dilute hydrochloric acid. The precipitate was filtered off and purified by recrystallization.

Compound **VIIa**. Yield 82%, mp 94–96°C (from ethanol). IR spectrum: ν 1730 cm^{-1} (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.3 t (3H, $CH_2C\mathbf{H}_3$), 2.6 s (6H, SCH_3), 4.40 q (2H, OCH_2), 8.8 s (1H, CH=N). Mass spectrum: *m*/*z* 316 $[M]^+$. Found, %: C 37.8; H 3.9; N 17.9; S 30.3. $C_{10}H_{12}N_4O_2S_3$. Calculated, %: C 38.0; H 3.8; N 17.7; S 30.4. *M* 316.42.

Compound **VIIb**. Yield 80%, mp 147–148°C (from methanol). IR spectrum, ν, cm^{-1}: 1700 (C=O, ester), 1660 ($C^{4'}$=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.5 t (3H, $CH_2C\mathbf{H}_3$), 2.6 s (3H, 3′-CH_3), 2.75 s (6H, SCH_3), 4.2 q (2H, OCH_2). Mass spectrum: *m*/*z* 358 $[M]^+$. Found, %: C 40.0; H 3.8; N 15.3; S 26.5. $C_{12}H_{14}N_4O_3S_3$. Calculated, %: C 40.2; H 3.9; N 15.6; S 26.8. *M* 358.27S.

Compounds VIIIa–VIIIc (*general procedure*). A mixture of 10 mmol of compound **VIIa**, **VIIb**, or **IX** and 20 mmol of hydrazine hydrate (80% w/w) in 20 ml of ethanol containing 4 drops of triethylamine was heated for 12 h under reflux. After cooling, the precipitate was filtered off and recrystallized from appropriate solvent.

5-Methylsulfanyl-4-([1,2,4]triazolo[3,4-*b*][1,3,4]-thiadiazol-6-yl)-2,3-dihydro-1*H*-pyrazol-3-one (VIIIa). Yield 55%, mp >300°C (from DMF). IR spectrum, ν, cm^{-1}: 3221 (NH), 1686 (CO). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.5 s (3H, SCH_3), 8.5 br.s (1H, NH), 9.1 s (1H, CH=N), 10.5 s (1H, NH). Mass spectrum: *m*/*z* 254 $[M]^+$. Found, %: C 33.0; H 2.3; N 33.2; S 25.3. $C_7H_6N_6OS_2$. Calculated, %: C 33.1; H 2.4; N 33.1; S 25.2 %. *M* 254.29.

5-Methylsulfanyl-4-(3-methyl-4-oxo-4*H*-[1,3,4]-thiadiazolo[2,3-*c*][1,2,4]triazin-7-yl)-2,3-dihydro-1*H*-pyrazol-3-one (VIIIb). Yield 75%, mp 295–297°C (from acetic acid). IR spectrum, ν, cm^{-1}: 3306–2927 br (NH); 1681, 1668 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.7 s (3H, 3′-CH_3), 2.8 s (3H, SCH_3), 8.5 br.s (1H, NH), 10.7 br.s (1H, NH). Mass spectrum: *m*/*z* 296 $[M]^+$. Found, %: C 36.6; H 2.6; N 28.1; S 21.3.$C_9H_8N_6O_2S_2$. Calculated, %: C 36.5; H 2.7; N 28.4; S 21.6. *M* 296.20.

4-(3-Methyl-4-oxo-4*H*-[1,3,4]thiadiazolo[2,3-*c*]-[1,2,4]triazin-7-yl)-2,3-dihydro-1*H*-pyrazol-3-one (VIIIc). Yield 50%, mp 234–235°C (from ethanol). IR spectrum, ν, cm^{-1}: 3280–3220 br (NH); 1675, 1660 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.7 s (3H, 3′-CH_3), 6.8 s (1H, 5-H), 10.5 s (1H, NH), 10.8 s (1H, NH). Found, %: C 38.2; H 2.3; N 33 3; S 12.5. Calculated , %: C 38.4; H 2.4; N 33.6; S 12.8.

Ethyl 3-dimethylamino-2-(3-methyl-4-oxo-4*H*-[1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazin-7-yl)acrylate (IX). *N*,*N*-Dimethylformamide dimethyl acetal, 10 mmol, was added dropwise over a period of 15 min to a solution of 10 mmol of compound **IIIb** in 20 ml of toluene under stirring at room temperature. The mixture was stirred for 3 h and evaporated to dryness under reduced pressure, and the residue (an oily material) was subjected to column chromatography using ethyl acetate as eluent. Yield 60%, mp 199–200°C,

R_f 0.25. IR spectrum, ν, cm^{-1}: 1664, 1617 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.4 t (3H, CH_2CH_3), 2.6 s (3H, 3′-CH_3), 3.1 s and 3.2 s (3H each, NCH_3), 4.0 q (2H, OCH_2), 8.2 s (1H, 3-H). Mass spectrum: *m*/*z* 309 $[M]^+$. Found, %: C 46.4; H 4.7; N 22.4; S 10.2. $C_{12}H_{15}N_5O_3S$. Calculated, %: C 46.6; H 4.9; N 22.6; S 10.4. *M* 309.28.

Phenyl([1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazol-6-yl)methyl 6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (XIa) and 3-methyl-4-oxo-4*H*-[1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazin-7-yl(phenyl)methyl 6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (XIb) (*general procedure*). A mixture of 10 mmol of D-Amygdalin (**X**) and 10 mmol of compound **I** or **II** in ethanol containing a catalytic amount of piperidine was heated for 12 h under reflux. The mixture was then evaporated to dryness, 30 ml of pyridine and 20 ml of acetic anhydride were added to the residue, and the mixture was stirred for 10 h at room temperature. The mixture was evaporated with addition of toluene, the residue was dissolved in chloroform, and the solution was washed in succession with hydrochloric acid, a saturated solution of sodium hydrogen carbonate (50 ml), and water (3× 50 ml), dried over anhydrous sodium sulfate, and evaporated. The residue was purified by column chromatography using hexane–ethyl acetate (1:1) as eluent (**XIa**, R_f 0.3; **XIb**, R_f 0.5).

Compound **XIa**. Yield 57%, white powder, mp 130–132°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.88–2.1 (21H, CH_3CO), 3.55 d.d (1H, 4a-H, $J_{3,4}$ = $J_{4,5}$ = 9.1 Hz), 3.61 d.d (1H, 2a-H, $J_{1,2}$ = $J_{2,3}$ = 9.5 Hz), 3.67–3.72 m (5H, 6b-H, 6b′-H, 5a-H, 4b-H, 6a-H), 3.88 m (1H, 5b-H), 4.00 d.d (1H, 3a-H, $J_{2,3}$ = 9.5, $J_{3,4}$ = 9.2 Hz, H-3a), 4.15 m (2H, 3b-H, 6a′-H), 5.30 d (1H, 1b-H, $J_{1,2}$ = 9.1 Hz), 5.69 d.d (1H, 2b-H, $J_{1,2}$ = $J_{2,3}$ = 9.1 Hz), 6.12 d (1H, 1a-H, $J_{1,2}$ = 9.5 Hz), 6.6 m (1H, PhC**H**), 7.2–7.5 m (5H, C_6H_5), 9.1 s (1H, CH=N). Found, %: C 50.70; H 4.8; N 6.5.$C_{36}H_{42}N_4O_{18}S$. Calculated, %: C 50.82; H 4.97; N 6.58 %.

Compound **XIb**. Yield 52%, pale yellow crystals, mp 152–154°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.9–2.2 (21H, CH_3CO), 2.5 s (3H, CH_3), 3.40–3.70 m (7H, 4a-H, 2a-H, 6b-H, 6b′-H, 5a-H, 4b-H, 6a-H), 3.9 m (1H, 5b-H), 4.1 d.d (1H, 3a-H, $J_{2,3}$ = 9.4, $J_{3,4}$ = 9.1 Hz), 4.20 m (2H, 3b-H, 6a′-H), 5.22 d (1H, 1b-H, $J_{1,2}$ = 9.2 Hz), 5.77 d.d (1H, 2b-H, $J_{1,2}$ = $J_{2,3}$ = 9.2 Hz), 6.30 d (1H, 1a-H, $J_{1,2}$ = 9.4 Hz), 6.7 m (1H, PhC**H**), 7.4–7.8 m (5H, C_6H_5). Found, %: C 51.00; H 4.8; N 6.1. $C_{38}H_{44}N_4O_{19}S$. Calculated, %: C 51.12; H 4.96; N 6.27.

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