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An efficient one-pot synthesis of pyrazolyl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazin-6-yl)-2*H*-pyran-2-one derivatives via multicomponent approach and their potential antimicrobial and nematicidal activities

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ABSTRACT

A series of simple or/and aryl, heteryl hydrazono pyrazolyl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazin-6-yl)-2*H*-pyran-2-one derivatives have been efficiently synthesized in excellent yields via one-pot, multi-component approach. The importance of this methodology is that in a one-pot operation four new bonds (3C–N and 1C–S) are generated. The structure of compound **5a** was confirmed by single-crystal X-ray diffraction. The newly synthesized compounds were evaluated for their in vitro antimicrobial activity against gram-positive bacteria (*Staphylococcusaureus* and *Bacillussubtilis*), gram-negative bacteria (*Escherichiacoli* and*Klebsiellapneumoniae*), antifungal activity against *Candida albicans*, and nematicidal activity against *Meloidogyneincognita*. Among all the compounds **6f** showed excellent antimicrobial and nematicidal activity against tested bacteria, fungi, and nematodes.

Multi-component reactions (MCRs) are processes 'in which more than two reactants directly get converted into their products by one-pot reaction.'[1] Remarkable features of MCRs exhibit higher atom economy and selectivity as well as produce fewer by-products compared to classical multistep synthesis.[2] Therefore, the discovery of novel protocols using multicomponent strategy has become an increasingly active area of research for generating biologically active poly-substituted nitrogen scaffolds for drug discovery program. The fused heterocyclic ring of triazoles and thiadiazines called triazolo-thiadiazines, which is the core structure of various synthetic nitrogen bridged heterocyclic systems exhibit various biological activities such as antibacterial, antifungal, antiviral, anti-tubercular, anti-helmintic, diuretic, analgesic, anti-tumor, anti-inflammatory, CNS-stimulant, PDE4 inhibitors, and hypoglycemic agents.[3] The 1,2,4-triazole group is a basicstructure in various marketed drugs, for example, Alprazolam,[4] Triazolam,[5] Etizolam,[6] and Furacylin.[7] Pyrazoles are found as key substructures in a large variety of compounds exhibiting activity such as analgesic, anti-inflammatory, antipyretic, muscle relaxant, anticonvulsant, hypertensive, anti-diabetic, and antibacterial.[8] 3-Acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one (Dehydroacetic acid) is a pyran derivative and exhibits high biological activity.[9] 4-Hydroxy-2-pyrones are considered as one important class of anti-HIV agents and exhibit a widerange of antifungal, antimicrobial, cytotoxic, neurotoxic activities[10] and Alzheimer's disease.[11]

The amino and mercapto groups are ready-made nucleophilic centers for the synthesis of condensed heterocyclic rings.[12] 4-Amino-5-hydrazino-4*H*-[1,2,4]triazole-3-thiols can be considered as useful synthons in preparing triazolo-thiadiazines. A survey of literature revealed that, 1,3,4-thiadiazines and triazolo-thiadiazines are prepared mainly based on the cyclocondensation of heterocyclic amino thiols with bifunctional reagents such as α-halo/tosyloxy carbonyl compounds, dihalides and α-halo nitriles.[13] However, most of these methods have drawbacks such as useof expensive, hazardous reagents, tedious work-up, purification procedures, high boiling solvents, and multi-step synthesis. Recently, some authors reported poly aza heterocyclic systems like 1,2,4-triazolo[3,4-*b*][1,3,4]-thiadiazine with 5-(benzofuran-2-yl)-1-phenylpyrazole nucleus along with their antimicrobial activity,[14] 1,2,4-triazolo[3,4-*b*][1,3,4]-thiadiazine with thiazolo[3,2-*a*]benzimidazole moiety,[15] and 3,6-diaryl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine analogs[16] as potential phosphodiesterase-4 inhibitors in NIH-3T3 mouse fibroblastic cells via multistep synthesis. However, to the best of our knowledge, this one-pot multi-component reaction fortri-heterocyclized pyrazolyl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazin-

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6-yl)-2*H*-pyran-2-one derivatives has been unprecedented to date. In view of these observations,[17] it was thought worthwhile to synthesize certain active pharmacophores, namely triazolo-thiadiazines and pyrazole in a single molecular framework which definitely shows significant biological activity.

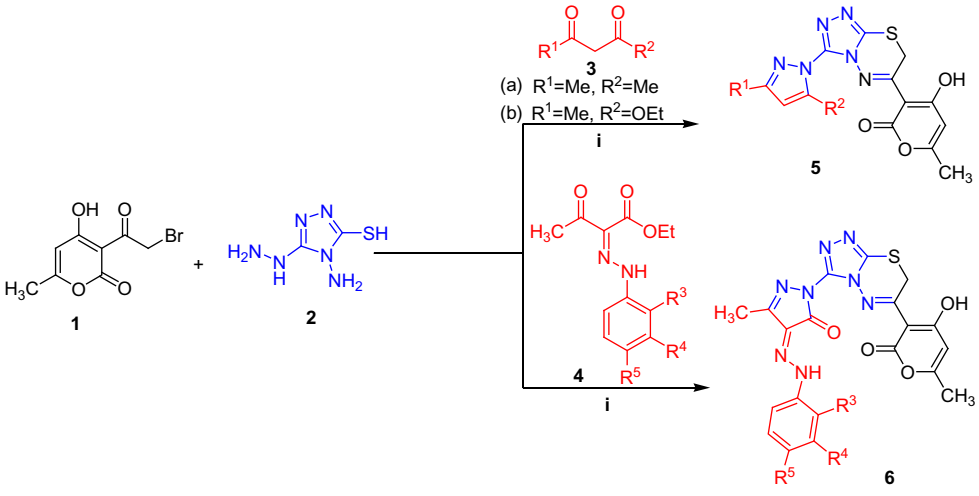
Herein, a facile method has been described for the synthesis of title products via one-pot transformation containing several reacting centers with NaOAc/MeOH as solvent (Scheme 1). Reaction of equimolar mixture of 3-(2-bromoacetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**1**) with 4-amino-5-hydrazino-4*H*-[1,2,4]triazol-3-thiol(**2**) and acetyl acetone/ethyl aceto acetate (**3**) or ethyl-2-(2-phenylhydrazono)-3-oxobutanoates (**4**) in NaOAc/MeOH under reflux conditions afforded the corresponding title products (**5a**) and (**6a**–**m**) in good to excellent yields. The scope and the generality of the present method were further demonstrated by the reaction of different derivatives of ethyl-2-(2-aryl, heteryl hydrazono)-3-oxobutanoates (Table-6, possessing both electron-donating and electron-withdrawing groups) with 3-(2-bromoacetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**1**) and 4-amino-5-hydrazino-4*H*-[1,2,4]triazol-3-thiol. The desired product was obtained in each case good to excellent yield. This work may trigger an interesting chemistry involving new methodology. The striking feature of the synthesisis that different hetero atom bonds like C–S, N=C, N–C, N=C (compound **5**) and C–S, N=C, N–C=O, and N=C (compound **6**) are formed simultaneously in one pot leading to selective novel hetero cyclization without formation of any other products.

During thiadiazine ring formation, the highly nucleophilic mercapto group of the 4-amino-5-hydrazino-4*H*-[1,2,4]triazole-3-thiol, attacks the carbon atom (CH_2–Br) of 3-(2-bromoacetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one to give a substituted intermediate. This undergoes further intra-molecular cyclization leading to the formation of 3-(3-hydrazino-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazin-6-yl)-4-hydroxy-6-methyl-pyran-2-one. This subsequently undergoes condensationreaction with acetyl acetone/ethylacetoacetate/different derivatives of ethyl-2-(2-arylhydrazono)-3-oxobutanoate (β-ketoester) to give end products **5** and **6** (Scheme 2).

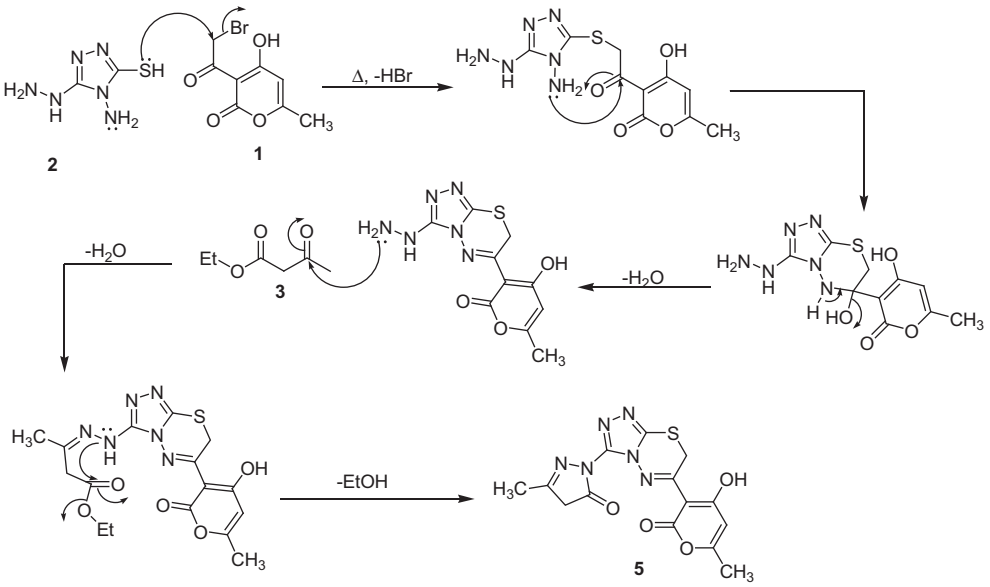
The structures of the newly synthesized compounds were confirmed by their spectral (IR, ^{1}H, ^{13}C NMR, and MS) and elemental analyses. For example, the IR spectrum of compound **5a** showed four strong absorption peaks at 1608 cm^{-1} for C=N, at 1707 cm^{-1} for lactone carbonyl and at 3367 cm^{-1} for OH. In the ^{1}H NMR spectra, singlets were observed for S–CH_2 of thiadiazine at δ 4.39, C-5 proton of pyran atδ 6.21 and pyrazole proton at δ 6.28. The ^{13}C NMR spectrum of **5a** shows the peaks at δ 11.3, 13.1, 19.5,and 171.7 for pyran methyl, pyrazole methyls, and S–CH_2 of thiadiazine and C=O of pyran, respectively. The IR spectrum of compound **6a** showed prominent peaks at 1610 cm^{-1} for C=N, at 1709 cm^{-1} for lactone carbonyl, at 3325 cm^{-1} for –NH, and 3437 cm^{-1} for –OH, whereas the ^{1}H NMR of compound **6a** showed characteristic singlets for S–CH_2 of thiadiazine at δ 4.21 and C-5 proton of pyran at δ 6.21. The –NH proton appeared as a broad singlet atδ 12.81. The ^{13}C NMR spectrum of **6a** shows the peaks at δ 11.6, 19.1, 24.5, and 170.8 for pyran methyl, pyrazole methyl, S–CH_2 of thiadiazine, and C=O of pyran, respectively. All the other aromatic protons of **6a**–**m** were observed at the expected regions. Mass spectra of the **6a** showed 499 $(M+H)^+$ peak in agreement with molecular formulae. Like this, the remaining spectral data confirmed the newly prepared compound structures (**5a, b**, and **6a**–**m**).

The average diameters of inhibition zones (IZ) of bacterial or fungal growth values are compared with those of standard antibiotic Kanamycin for bacteria and Clotrimazole forfungus. From Table 3 it should be noted that, four compounds **6a**, **6e**, **6f**, and **6g** were found to be most potent members showing zone of inhibition against all the bacterial and fungal strains. And also, **6f** was found to be most effective against all the tested bacteria and fungi showing maximum zone of inhibition 28.0, 24.0, 35.0, 34.0, and 27.0 mm even greater than the standard drug Kanamycin and Clotrimazole. However, compounds **5a**, **5b**, **6b**, **6c**, **6d**, **6h**, **6i**, and **6k** exhibit moderate activity and compounds **6j**, **6l**, and **6m** have not shown the activity. From the minimum inhibitory concentrationstudies (MIC), Table 4 compound **6f** was identified as the most potent inhibitor with significant MIC values of 8.0, 10.0, 10.0, 6.0, and 11.0 μg/mL which are more or equal to the standard drugs. The antimicrobial activity data reveal that compounds containing 3-nitro group on the phenyl (**6f**) ring, were showing excellent activity against the tested bacteria and fungi. Compounds **6a**, **6e**, and **6g** are showing good activity and the remaining compounds showing moderate activity against all the tested bacterial and fungal strains. The nematicidal activity experiments were performed according to the literature procedure[18] and tested for against *Meloidogyneincognita*.

Effect of diluted compounds on mortality of *Meloidogyne incognita* at different time intervals. From the results, (Table 5) the compounds **6f** and **6g** were found to be most active, as it caused 67–85% and 52–73% mortality of the nematode larvae after an exposure of 24 and 48 h. Compounds **6a**, **6c**, **6d**, and **6e** were found to posses good activity as these caused only 42–55%, 35–51%,



Scheme 1. Reagents and conditions: (**i**) MeOH, fused AcONa, reflux 4 h, 85 °C.



Scheme 2. The plausible mechanism for the formation of products.

Table 3
Antibacterial and antifungal activity of compounds **5a**, **b**, and **6a–m**

Compound numbers	Zone of inhibition in mm				
	Gram-negative bacteria		Gram-positive bacteria		Fungi
	E. coli	*K. pneumoniae*	*S. aureus*	*B. subtilis*	*C. albicans*
5a	8	8	8	8	8
5b	8	8	9	8	8
6a	16	16	15	16	16
6b	8	8	8	8	8
6c	10	10	9	9	9
6d	11	10	9	9	9
6e	17	15	14	10	10
6f	28	24	35	27	27
6g	20	17	18	19	19
6h	8	8	8	8	8
6i	8	8	8	8	8
6j	—	—	—	—	—
6k	10	13	8	8	8
6l	—	—	—	—	—
6m	—	—	—	—	—
Kanamycin	25	23	32	—	—
Clotrimazole	—	—	—	—	25

Table 4
Minimum inhibitory concentration studies

Compound numbers	MIC (μg/mL)				
	Gram negative bacteria		Gram positive bacteria		Fungi
	E. coli	*K. pneumoniae*	*S. aureus*	*B. subtilis*	*C. albicans*
5a	80	80	80	80	80
5b	80	80	80	80	80
6a	25	33	35	25	30
6b	80	80	80	76	80
6c	50	50	55	50	60
6d	45	55	50	50	55
6e	14	22	27	19	27
6f	08	10	10	6	11
6g	18	23	24	20	20
6h	75	75	75	75	75
6i	75	75	75	75	75
6j	—	—	—	—	—
6k	75	63	65	65	70
6l	—	—	—	—	—
6m	—	—	—	—	—
Kanamycin	8	11	10	4	—
Clotrimazole	—	—	—	—	10

18–28%, and 40–44% mortality after the exposure where as compounds **5a** (5–8%), **5b** (5–9%), **6b** (8–11%), **6h** (5–8%), **6i** (5–9%), **6j** (5–8%), **6k** (5–12%), **6l** (3–5%), and **6m** (2–3%) were found to be least active.All compounds indicated time and concentration dependent activity. The activity was higher at high concentrations and increased with time. There was no mortality observed in the control.

In this work an efficient methodology for the synthesis of triheterocyclized pyrazolyl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazin-6-yl)-2*H*-pyran-2-one derivatives has been described via one-pot, multicomponent reaction and evaluated for their antimicrobial activity against gram-positive, gram-negative bacteria, fungi, and nematodes. Finally, the structure of **5a** was confirmed unambiguously by single crystal X-ray diffraction analysis. Among them compound **6f** showed excellent activity against bacteria, fungi, and nematodes. Thus, compound **6f** was considered to be a lead analog for subsequent optimization in the search for novel antimicrobial agents.

3-(2-Bromoacetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one[19] and ethyl-2-(2-arylhydrazono)-3-oxobutanoates[20] were prepared by the literature procedure. The antimicrobial cell susceptibility testing was performed by agar disk-diffusion technique according to Bauer et al. 1966.[21,22] a standard Kanamycin[23] (30 μg/disk) against bacteria and Clotrimazole[24] (10 μg/disk) against fungi. MIC of the synthesized compounds was determined using the method described by Villanova 1982.

*General procedure for the synthesis of compounds(**5a**, **b**,**and6a–m**):* 3-(2-Bromoacetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (0.001 mol), 4-amino-5-hydrazino-4*H*-[1,2,4]triazol-3-thiol (0.001 mmol), and acetyl acetone/EAA (0.001 mol) or different derivatives of ethyl-2-(2-arylhydrazono)-3-oxobutanoates (0.001 mol) were taken in 5 mL of methanol, then fused sodium acetate (2 mmol) was added to the mixture. The resultant mixture was refluxed for 4 h. After completion of the reaction (monitored with TLC), the reaction mixture was cooled to rt. The solid was formed gradually. It was filtered,

Table 5
Nematicidal activity

Compound numbers	24 h			48 h		
	250 (μg/mL)	150 (μg/mL)	50 (μg/mL)	250 (μg/mL)	150 (μg/mL)	50 (μg/mL)
5a	5	3	2	8	5	4
5b	5	3	2	9	6	4
6a	42	28	15	55	33	26
6b	8	5	2	11	6	3
6c	35	20	10	51	28	19
6d	18	10	6	28	16	10
6e	40	23	19	44	28	20
6f	67	43	32	85	63	45
6g	52	35	20	73	55	28
6h	5	3	1	8	5	3
6i	5	3	2	9	5	3
6j	5	3	2	8	6	3
6k	5	3	2	12	5	3
6l	3	0	0	5	2	0
6m	2	0	0	3	2	0
DMSO	0	0	0	0	0	0

washed with water, dried, and purified by recrystallization from absolute ethanol.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.07.148.

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