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INVESTIGATION OF THE REACTION OF 3-[2-OXO-2-(2-THIENYL)ETHYLIDENE] INDOL-2(1*H*)-ONES WITH 2-HYDRAZINOBENZIMIDAZOLE AND EVALUATION OF INSECTICIDAL ACTIVITY

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ABSTRACT:The reaction of 3-[2-oxo-2-(2-thienyl)ethylidene] indol-2(1*H*)-one (**1**) with 2-hydrazinobenzimidazole (**2**) in different media and solvent have been investigated. The impact of substituent on indolyl nitrogen was also studied. The reaction of (**1**) and (**2**) in ethanol with acetic acid gave 3-thienoyl (2-benzimidazolyl hydrazono)methylene-indole -2 (1*H*) ones (**3** ; when indolyl>NH is substituted). Reaction of 1 and 2 in ethanol with diethylamine yielded 3-benzimidazolyl-1-thienyl-9*H*-pyridazino [3,4-*b*] indole (**4** ; when indolyl >NH is not substituted). Further, reaction of **1** and **2** in 2,2,2-trifluoroethanol media gave 1'-benzimidazolyl-5' thienyl-2',4'-dihydrospiro[indole-3,5'-pyrazol]-2(1*H*) ones (**5**) irrespective of indolyl >NH substituted or unsubstituted.The structure of synthesized compounds were characterized by spectral (IR, ^{1}H-NMR, ^{13}C- NMR, Mass) and analytical data. Synthesized compounds were evaluated for insecticidal activity against *Periplanata americana* using Cypermethrin as standard and found to exhibit excellent results.

KEYWORDS :3-Thienoyl (2-benzimidazolylhydrazone) methylene- indole 2 (1*H*) ones, 3-benzimidazolyl-1-thienyl-9*H*-pyridazino [3,4-*b*] indole, 2,2,2-trifluoroethanol, spiro[indol-3,3'-pyrazol]- 2 (1*H*) ones, insecticidal activity.

INTRODUCTION :

Isatin is a crucial pharmacological active compound and exihibit therapeutic importance such as analgesic,[i]anticancer,[ii]antitubercular,[iii]antiviral,[iv]antifungal,[v]and represents an important class of heterocyclic compounds which are used as a precursor for the synthesis of many useful drugs.[vi,vii]

Pyrazoline being a versatile molecule provides enormous prospects for the researchers to afford fruitful derivatives with superior pharmacological activity. The pharmacological profile of new generation pyrazoline derivatives provides a prolific matrix for the enhancement of existing medicinal compound potency.[viii]

Benzimidazole is a heterocyclic compound known for its antibacterial,[ix]antifungal,[x] anti-inflammatory [xi] and antiviral activities.[xii] Some studies have also shown that benzimidazole-containing drugs have good antitumor activity.[xiii]

In addition, pyrazoline derivatives have been reported to possess anticancer, antimicrobial and anti-inflammatory activities.[xiv]It was assumed that combining effect of indoles, benzimidazole and pyrazole in single molecule might result in the formation of some novel molecules with enhanced biological activities.[xv]

The development of practical, atom-economic and environmentally benign chemical reactions has become a vital consideration in current chemical research. Over the past two decades, the fluorinated alcohols have been recognized as magic solvents in a variety of reactions owing to their unique properties such as low nucleophilicity, strong hydrogen-bond donating ability, mild activity and high ionization power.[xvi,xvii]

Reaction of indole 2,3-diones with 2-thienyl acetophenone gave 3-hydroxy-3(2-oxo-2-thienyl)ethylindole-2-ones. Which on further dehydration with HCl and CH_3COOH furnishd 3[2-oxo-2-(2-thienyl)ethylidene]indole-2-ones(**1**).[xviii] These compounds are highly reactive due to presence of an alkene system flanked by carbonyl group. The nature of solvent and substituent on nitrogen atom of indole plays significant role in the formation of products.[xix,xx]

We, herein reporting the reaction of 3-[2-oxo-2(thienyl)ethyledene]indol-2-ones (**1**) with 2-hydrazinobenzimidazole (**2**) for the first time. Currently challanges to built up innovative organic transformation that are not only efficient selective and high yielding but also environmentally benign make the choice of suitable reaction medium necessary for triumphant synthesis.

The reaction of chalcone (**1**) with various compounds eg. H_2O_2[xviii] and 2-hydrazinobenzothiazoles[xvii] have recently been investigated by us, however the reaction with 2-hydrazinobenzimidazole has not so far been studied.

The reaction of **1** and **2** in ethanol with acetic acid gave 3-thienoyl (2-benzimidazolylhydrozono) methylene-indole-2 (1*H*) ones (**3**; when indolyl H is substituted). While the reaction of **1** and **2** in ethanol with diethylamine gave 3-benzimidazolyl-1-thienyl-9*H*-pyridazino [3,4-*b*] indole (**4**; when indolyl H is not substituted).

Prompted by green credentials of fluorinated alcohols reaction of (**1**) in 2,2,2-trifluoroethanol with 2-hydrazinobenzimidazole (**2**) gave 1-benzimidazolyl-5'-thienyl-2',4'-dihydrospiro[indole-3,3'-pyrazole]-2(1*H*) ones (**5**) **(Scheme-1)**. Furthermore, newly synthesized compounds were evaluated for insecticidial activity against *Periplanata americana* using Cypermethrin as standard.

MATERIALS AND METHODS :

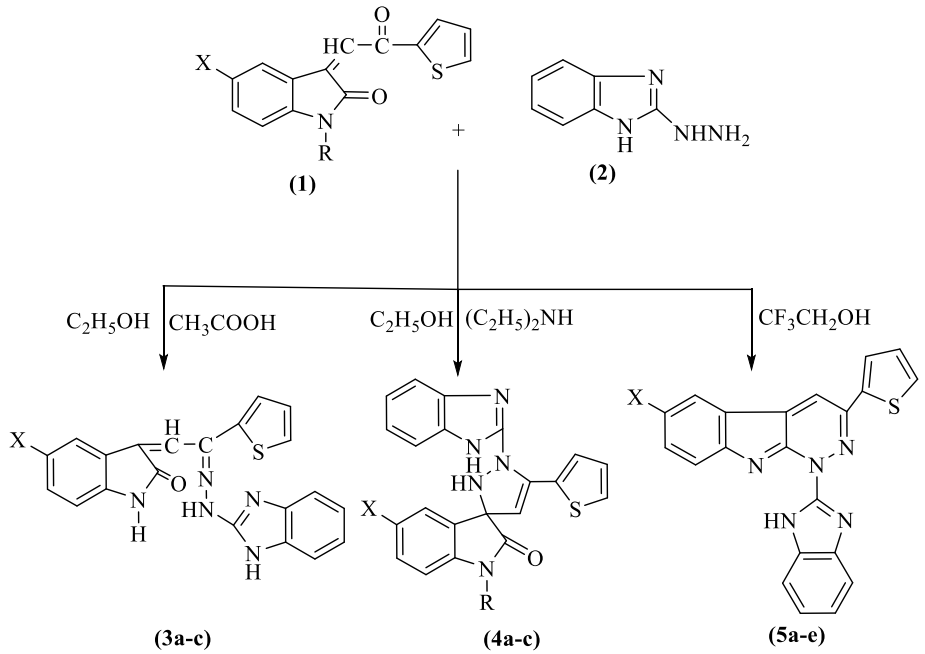
Chemistry

Melting points are uncorrected and were taken in open glass capillaries using a Gallenkamp melting point apparatus. The IR spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer in KBr pellets and band positions are recorded in wavenumbers (cm^{-1}). ^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ with TMS as an internal reference on a JEOL spectrometer at 300 and 75 MHz, respectively. The mass spectra were recorded on XEVO G2S QTOF-YDA220 mass spectrometer. The elemental analyses were performed at Central Drug Research Institute, Lucknow, India. Chemicals were purchased from Acros Organics and used without further purification. 2-hydrazinobenzimidazole was prepared following literature method.[xxi]

General procedure for synthesis of 3-thienoyl (2-benzimidazolylhydrazono)methylene-indol- 2(1*H*)-ones (3a-c).

Equimolar quantities of 3-[2-oxo-2-(2-thienyl)ethylidene]indol-2(1*H*)-ones **(1**,0.01 mol) and 2-hydrazinobenzimidazole **(2,** 0.01 mol) were dissolved in absolute alcohol (10.0 mL) and

acetic acid (1.0 mL) added as a catalyst and reaction mixture was refluxed for an appropriate time (4-5 hours).The completion of the reaction was monitored by TLC. The reaction mixture was cooled at room temperature and the resultant solid precipitate was filtered and washed with ethanol to furnished pure products **3a-c**.



Compounds	X	R	Compounds	X	R
3a	H	CH_3	**5a**	H	H
3b	H	C_2H_5	**5b**	F	H
3c	H	CH_2Ph	**5c**	H	CH_3
4a	H	H	**5d**	H	C_2H_5
4b	F	H	**5e**	H	CH_2Ph
4c	Cl	H	-		

Scheme 1 : Synthesis of compounds (**3a-c**), (**4a-c**) and (**5a-e**).

1-Methyl-3-thienoyl(2-benzimidazolylhydrazono)methylene- indol- 2(1*H*)-one (3a).
Yield : 92 %; M.P. : 270-272°C; IR (KBr, υ_{max} , cm^{-1}):3410 (NHN),3340 (NH), 1680 (C=O), 1630 (C=N);^{1}H-NMR (δ, $CDCl_3$+DMSO-d_6, 300.15 MHz) :3.42 (s, 3H, NCH_3), 6.12 (s, 1H, =CH), 6.68–7.89(m, 11H,Ar-H), 8.86 (s, 1H, NH), 9.78 (s, 1H, NHN); ^{13}C-NMR (δ, $CDCl_3$+DMSO-d_6, 75.47 MHz) : 34.8 (NCH_3), 122.1(=CH), 117.9, 118.32, 119.09, 120.67, 121.01, 122.33, 126.08, 128.33, 129.74, 130.9, 131.69, 131.77, 132.89, 133.50, 134.79, 135.20, 136.30, 137.50 (Ar-C), 149.20 (C=N), 189.30 (CO). MS. Calcd. For $C_{22}H_{17}N_5OS$:399.4732 Found : 399.4737. Anal. Calcd for $C_{22}H_{17}N_5OS$: C, 66.15; H, 4.28; N, 17.53%. Found : C, 66.18; H, 4.25; N, 17.57%.

1-Ethyl-3-thienoyl (2-benzimidazolylhydrazono)methylene-indol- 2(1*H*)-one (3b).
Yield : 90 %; M.P. : 275-277 °C; IR (KBr, υ_{max} , cm^{-1}):3405 (NHN), 3350 (NH), 1680 (C=O), 1630 (C=N);^{1}H-NMR (δ, $CDCl_3$+DMSO-d_6, 300.15 MHz) :1.65 (t,J=7.25 Hz, 3H, CH_3), 3.86 (q, J=7.25 Hz,2H, -NCH_2), 6.20 (s, 1H, =CH), 6.65–7.85 (m, 11H, Ar-H), 8.85 (s, 1H, NH), 9.76 (s, 1H, NHN); ^{13}C-NMR (δ, $CDCl_3$+DMSO-d_6, 75.47 MHz) : 18.20(NCH_2**CH_3**), 44.20

(N**CH**$_2$CH$_3$),122.54(=CH-),117.8 118.40, 119.25, 120.70, 121.04, 122.36, 126.10, 128.36, 129.78, 130.8 131.70, 132.85, 133.60, 134.77, 135.40 136.90, 137.30, 138.50, (Ar-C) , 148.80(C=N), 188.62 (CO). MS. Calcd. For $C_{23}H_{19}N_5OS$: 413.5023 Found : 413.5025. Anal. Calcd for $C_{23}H_{19}N_5OS$: C, 66.81; H, 4.63; N, 16.93 %. Found : C, 66.83; H, 4.60; N, 16.97 %.

1-Benzyl-3-thienoyl (2-benzimidazolylhydrazono)methylene-indol- 2(1*H*)-one (3c).
Yield : 92%; M.P. : 279-281°C; IR (KBr, υ_{max} , cm^{-1}):3410 (NHN), 3345 (NH), 1670(C=O), 1630 (C=N);^{1}H-NMR (δ, $CDCl_3$+DMSO-d_6, 300.15 MHz) :4.01 (s, 2H, CH_2), 6.15 (s, 1H, =CH), 6.80–7.89 (m, 16H, Ar-H), 8.82 (s, 1H, NH), 9.80 (s, 1H, NHN); ^{13}C-NMR (δ, $CDCl_3$+DMSO-d_6, 75.47 MHz) : 49.50 (N-CH_2), 122.48 (=CH), 117.50,118.68 118.46, 119.25,119.52, 120.70, 121.04,121.24,123.81 122.36, 126.10, 128.36, 129.78, 130.8 131.70, 132.16,132.85, 133.60,134.28, 134.67, 135.42 136.89, 137.35, 138.50, (Ar-C) ,148.90(C=N), 189.10(CO). MS. Calcd. For $C_{28}H_{21}N_5OS$: 475.5736 Found : 475.5730. Anal. Calcd for $C_{28}H_{21}N_5OS$:C, 71.72; H, 4.45; N, 14.73 %. Found : C, 71.70; H, 4.48; N, 14.75 %.

3-Benzimidazolyl-1-thienyl-9*H*-pyradizino(3,4-b)indoles(4a-c).

Equimolar quantities of 3-[2-oxo-2-(2-thienyl)ethylidene]indol-2(1*H*)-ones **(1**,R=H**,** 0.01 mol) and 2-hydrazinobenzimidazole **(2,** 0.01 mol) were dissolved in absolute alcohol (10.0 mL) and acetic acid (1.0 mL) added as a catalyst and reaction mixture was refluxed for an appropriate time (30-45 minutes).The completion of the reaction was monitored by TLC. The reaction mixture was cooled at room temperature and the residue was chromatographed (Silica gel 200-300 mcs; eluent pet ether:EtOAc, 5:5) to afford pure products**4a-c**.

3-Benzimidazolyl-1-thienyl-9*H*-pyradizino(3,4-b)indole (4a).
Yield : 90 %; M.P. : 233-235°C; IR (KBr, υ_{max} , cm^{-1}):3330 (NH), 1620 (C=N);^{1}H-NMR (δ, $CDCl_3$+DMSO-d_6, 300.15 MHz) :6.55–7.85 (m, 12H, Ar-H), 8.65 (s, 1H, NH); ^{13}C-NMR (δ, $CDCl_3$+DMSO-d_6, 75.47 MHz) : 115.20,116.90, 118.02, 119.06, 120.60, 121.08, 122.36, 126.88, 128.13, 129.74, 130.92, 131.69, 131.70, 132.79, 133.52, 134.75, 135.22, 136.30, 137.54,138.12,140.20 (Ar-C). MS. Calcd. For $C_{21}H_{13}N_5S$: 367.4330 Found : 367.4328. Anal. Calcd for $C_{21}H_{13}N_5S$: C, 68.64; H, 3.56; N, 19.06 %. Found : C, 68.67; H, 3.59; N, 19.10 %.

3-Benzimidazolyl-5'-fluoro-1-thienyl-9*H*-pyradizino(3,4-b)indole (4b).
Yield : 88 %; M.P. : 230-232°C; IR (KBr, υ_{max} , cm^{-1}):3320 (NH),1620 (>C=N);^{1}H-NMR (δ, $CDCl_3$+DMSO-d_6, 300.15 MHz) :6.55–7.86 (m, 11H, Ar-H), 8.62 (s, 1H, NH); ^{13}C-NMR (δ, $CDCl_3$+DMSO-d_6, 75.47 MHz) : 115.60,116.92, 118.12, 119.06, 120.60, 121.08, 122.86, 126.80, 128.23, 129.24, 130.90, 131.70, 131.78,132.89, 133.50, 134.78, 135.25,136.32, 137.64,138.22,139.80(Ar-C). MS Calcd. For $C_{21}H_{12}FN_5S$: 385.4238 Found : 385.4234. Anal. Calcd for $C_{21}H_{12}FN_5S$: C, 66.44; H, 3.14; N, 18.13 %. Found : C, 66.48; H, 3.18; N,18.13 %.

3-Benzimidazolyl-5'-chloro-1-thienyl-9*H*-pyradizino(3,4-b)indole (4c).
Yield : 89 %; M.P. : 237-239°C; IR (KBr, υ_{max} , cm^{-1}):3320 (NH), 1620 (>C=N);^{1}H-NMR (δ, $CDCl_3$+DMSO-d_6, 300.15 MHz) :6.55–7.85 (m, 11H, Ar-H), 8.64 (s, 1H, NH); ^{13}C-NMR (δ, $CDCl_3$+DMSO-d_6, 75.47 MHz) : 115.40,116.79, 118.52, 119.26, 120.61, 121.18, 122.38, 126.98, 128.23, 129.76, 130.93, 131.67, 131.72, 132.78, 133.55, 134.85, 135.25, 136.20, 137.84,138.22,140.30 (Ar-C). MS. Calcd. For $C_{21}H_{12}ClN_5S$: 401.8784 Found : 401.8780. Anal. Calcd for $C_{21}H_{12}ClN_5S$: C, 62.76; H, 3.01; N, 17.42 %. Found : C, 62.78; H, 3.04; N, 17.39 %

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General procedure for the synthesis of 1'-Benzimidazolyl-5'-thienyl-2'-4'-dihydrospiro[indole-3,3'-pyrazole]- 2(1*H*)-ones (5a-e).

Equimolar quantities of 3-[2-oxo-2-(2-thienyl)ethylidene]indol-2(1*H*)-ones **(1**,0.01 mol) and 2-hydrazinobenzimidazole **(2,** 0.01 mol) in 2,2,2-trifluoroethanol (10.0 mL) was refluxed for an appropriate time (30-45 minutes).The completion of the reaction was monitored by TLC. The solid precipitate was filtered and washed with trifluoroethanol to furnished pure products **5a-e**. The trifluoroethanol was distilled off to recover for the next reaction.

1'-Benzimidazolyl-5'-thienyl-2'-4'-dihydrospiro[indole-3,3'-pyrazole]- 2(1*H*)-ones (5a).
Yield : 92 %; M.P. : 288-290 °C; IR (KBr, υ_{max} , cm^{-1}):3400 (NH), 3300 (NH), 3290 (NH of pyrazole), 1680 (CO of indole);^{1}H-NMR (δ, $CDCl_3$+DMSO-d_6, 300.15 MHz) :6.25 (s, 1H,=CH),6.80-7.89 (m, 11H, Ar-H), 8.05 (s, 1H, NH of pyrazole), 8.85 (s, 1H, NH of benzimidazole), 9.41 (s, 1H, NH of indole) ; ^{13}C-NMR (δ, $CDCl_3$+DMSO-d_6, 75.47 MHz) : 110.40 (spiro-C),128.60 (=CH of pyrazole), 118.20, 119.20, 120.01, 121.48, 122.42, 126.88, 128.25,129.71,130.92,131.66,132.88,133.50,134.65,135.28,136.21,137.24,138.28,141.80(Ar-C), 191.20 (CO). MS. Calcd. For $C_{21}H_{15}N_5OS$: 385.4485 Found : 385.4481. Anal. Calcd for $C_{21}H_{15}N_5OS$: C, 66.44; H, 3.92; N, 18.17 %. Found : C, 66.41; H, 3.96; N, 18.19 %.

1'-Benzimidazolyl-5-fluoro-5'-thienyl-2'-4'-dihydrospiro[indole-3,3'-pyrazole]- 2(1*H*)-ones (5b).
Yield : 93 %; M.P. : 280-282°C; IR (KBr, υ_{max} , cm^{-1}):3410 (NH), 3300 (NH), 3290 (NH of pyrazole), 1685(CO of indole);^{1}H-NMR (δ, $CDCl_3$+DMSO-d_6, 300.15 MHz) :6.30 (s, 1H,=CH),6.85-7.85 (m, 10H, Ar-H), 8.10 (s, 1H, NH of pyrazole), 8.86 (s, 1H, NH of benzimidazole), 9.40 (s, 1H, NH of indole); ^{13}C-NMR (δ, $CDCl_3$+DMSO-d_6, 75.47 MHz) : 109.80 (spiro-C), 128.50 (=CH of pyrazole), 117.80, 119.00, 120.09, 121.28,122.02, 126.78, 128.21,129.75,130.72,131.63,132.78,133.52,134.61,135.18,136.01,137.34,138.48,140.90(Ar-C), 190.90 (CO). MS. Calcd. For $C_{21}H_{14}FN_5OS$: 403.4390 Found : 403.4388. Anal. Calcd for $C_{21}H_{14}FN_5OS$: C, 62.52; H, 3.49; N, 17.36 %. Found : C, 62.55; H, 3.51; N, 17.32 %.

1'-Benzimidazolyl-1-methyl-5'-thienyl-2'-4'-dihydrospiro[indole-3,3'-pyrazole]- 2(1*H*)-ones (5c).
Yield : 91 %; M.P. : 283-285°C; IR (KBr, υ_{max} , cm^{-1}): 3300 (NH), 3280 (NH of pyrazole), 1680 (CO of indole);^{1}H-NMR (δ, $CDCl_3$+DMSO-d_6, 300.15 MHz) :3.40 (s, 3H, NCH_3),6.20 (s, 1H,=CH),6.75-7.89 (m, 11H, Ar-H), 8.12 (s, 1H, NH of pyrazole), 8.84 (s, 1H, NH of benzimidazole) ; ^{13}C-NMR (δ, $CDCl_3$+DMSO-d_6, 75.47 MHz) : 34.60 (NCH_3) ,110.20 (spiro-C),128.40 (=CH of pyrazole), 118.40, 119.20, 120.06, 121.23, 122.52, 127.00, 128.20, 129.05, 130.62, 131.10, 132.58, 133.32, 134.69, 135.28, 136.41, 137.44,138.52,140.90 (Ar-C), 190.80 (CO). MS. Calcd. For $C_{22}H_{17}N_5OS$:399.4732 Found : 399.4736. Anal. Calcd for $C_{22}H_{17}N_5OS$: C, 66.15; H, 4.28; N, 17.53 %. Found : C, 66.18; H, 4.29; N, 17.50 %.

1'-Benzimidazolyl-1-ethyl-5'-thienyl-2'-4'-dihydrospiro[indole-3,3'-pyrazole]- 2(1*H*)-ones (5d).
Yield : 90 %; M.P. : 285-287°C; IR (KBr, υ_{max} , cm^{-1}): 3310 (NH), 3270 (NH of pyrazole), 1680 (CO of indole);^{1}H-NMR (δ, $CDCl_3$+DMSO-d_6, 300.15 MHz) :1.82 (t , J=7.25 Hz, 3H, CH_3), 4.01 (q,J=7.25 Hz, 2H, N-CH_2), 6.18 (=CH), 6.78-7.88 (m, 11H, Ar-H), 8.08 (s, 1H, NH of pyrazole), 8.81 (s, 1H, NH of benzimidazole); ^{13}C-NMR (δ, $CDCl_3$+DMSO-d_6, 75.47 MHz) : 18.81 (NCH_2**CH_3**), 44.60 (N**CH_2**CH_3), 110.40 (spiro-C), 128.51 (=CH of pyrazole),118.20, 119.25, 120.26, 121.29, 122.42, 126.02, 128.28, 129.25, 130.63, 131.12, 132.78, 133.35

134.78, 135.30, 136.46, 137.40,138.56,141.50 (Ar-C), 191.20 (CO). MS. Calcd. For $C_{23}H_{19}N_5OS$:413.5023 Found : 413.5020. Anal. Calcd for $C_{23}H_{19}N_5OS$: C, 66.81; H, 4.63; N, 16.94 %. Found : C, 66.84; H, 4.60; N, 16.91 %.

1'-Benzimidazolyl-1-benzyl-5'-thienyl-2'-4'-dihydrospiro[indole-3,3'-pyrazole]- 2(1*H*)-ones (5e).

Yield : 90 %; M.P. : 290-292°C; IR (KBr, υ_{max} , cm^{-1}): 3305 (NH), 3280 (NH of pyrazole), 1685(CO of indole);^{1}H-NMR (δ, $CDCl_3$+DMSO-d_6, 300.15 MHz) :4.08 (s, 2H, N-CH_2), 6.22 (s,1H,=CH),6.80-7.90 (m, 15H, Ar-H),8.06(s, 1H, NH of pyrazole),8.86 (s,1H,NH of benzimidazole); ^{13}C-NMR (δ, $CDCl_3$+DMSO-d_6, 75.47 MHz) : 48.60 (NCH_2),110.50 (spiro-C),128.20 (=CH) ,117.80,118.82,119.24,120.16,121.30, 122.32,123.70,124.15,124.80,125.88 126.32,127.08, 128.28, 129.35, 130.28 131.32, 132.88, 133.75 134.85, 135.40, 136.96, 137.41,138.86,141.60 (Ar-C), 190.60 (CO). MS. Calcd. For $C_{28}H_{21}N_5OS$:475.5736 Found : 475.5732. Anal. Calcd for $C_{28}H_{21}N_5OS$: C, 71.72; H, 4.45; N, 14.72 %. Found : C, 71.75; H, 4.42; N, 14.76 %.

RESULTS AND DISCUSSION :

Chemistry

Theoretically this reaction offers three different possibilities (**Scheme 1**), *viz.*, formation of hydrazones**(3**), pyridazino derivatives (**4**) as well as spiro[indole-pyrazole] (**5**)depending on the site of condensation. The products formed dependent on the nature of solvent, medium and substitution on indolyl nitrogen.

The reaction of 3-[2-oxo-2-(2-thienyl)ethylidene]indol-2-ones (**1**) with 2-hydrazinobenzimidazole (**2**) in ethanol with acetic acid gives exclusively the hydrazones **3**, when indolyl >NH is substituted. Reaction of **1** and**2** in ethanol with diethylamine, when indolyl >NH is not substituted, can react with the enolic form of **2**eliminating water molecule gave the condenced product,pyridazino derivatives**4**. Alternatively, nucleophilic Michael addition of **1**and **2** in 2,2,2-trifluoroethanol medium gave spiro compounds**5** withoutaffecting the nature of substituent on indolyl nitrogen.

Exploration for the formation of products is based on spectral and analytical analysis. The formation of hydrazone derivatives, compound **3a**was confirmed by their IR spectrum which shows absorption band at 3410 cm^{-1} (-NHN), 3340 cm^{-1} (-NH of benzimidazole) and 1680 due to >C=O of indolering along with band at 1630 due to >C=N. In the ^{1}H NMR spectrum peaks appeared at δ 3.42 ppm for NCH_3, 6.12 ppm for =CH , 6.68-7.89 ppm multiplet due to aromatic protons, 8.86 ppm for -NH of benzimidazolyl ring and 9.78 ppm for -NHN=. ^{13}C NMR of **3a** exhibited peaks at δ 34.8, 122.10, 117.90-137.50, 149.20 and 189.30 ppm due to the NCH_3, =CH, aromatic carbons, C=N and C=O of indole ring carbons respectively. Further, in the mass spectrum molecular ion peak appeared at m/z 399.4737 (M^+).

The chemical structure of pyridazino derivatives (**4a**) was proven by their spectral characteristic marked by the disappearance of the absorption band due to >NHN- and carbonyl groups in the IR spectrum and appearance of =CH peak in the aromatic region at δ6.55-7.85 ppm in its ^{1}HNMR spectrum.The structure was further confirmed by mass spectrum, where molecular ion peak appeared at m/z 367.4328(M^+) corresponds to the molecular mass.

In the IR spectrum of **5a** absorption bands at 3300 and 3290 cm^{-1} due to –NH of indole and pyrazole respectively appeared and at 1680 cm^{-1} due to >C=O of indolewas observed. In its ^{1}HNMR spectrum signal appeared atδ6.25 ppm due to pyrazolyl =CH, δ 8.05 due to pyrazolyl >NH, δ 8.85 benzimidazolyl >NH, δ 9.41 ppm due to indolyl >NH and δ 6.80-7.89 ppm due to aromatic protons. ^{13}C NMR spectrum exhibited peaks at δ 110.4 ppm due to spiro carbon,128.60 due to =CH of pyrazole, 118.20-141.80 due to aromatic carbons and 191.20

due to >C=O of indole. The structure was further confirmed by mass spectrum, where molecule ion peak appeared at m/z 385.4481 (M^+) corresponded to the molecular mass.

INSECTICIDAL ACTIVITY

The synthesized **3a-c**,**4a-c** and **5a-e**were screened for their insecticidal activity following the literature method[xxii,xxiii] using *Periplaneta americana* (cockroach)and results were compared with the control drug (Cypermethrin).

Results and discussion

For insecticidal activity[xxii,xxiii], *Periplaneta americana* (cockroach) was taken due to its easy availability and wide use in such studies. Consequently 1% and 2% solutions in DMF of synthesized compounds were injected into the abdominal region of the cockroach with the help of micro syringe. At the time of death antennae became motionless, the appendages shrank and folded towards the central side and the cockroach lay dorsally which was noted as the Knock down (KD) value. The KD value of synthesized heterocyclic derivatives (**3a-c**, **4a-c**, **5a-e**) were compared with control drug (Cypermethrin). The results obtained are recorded in **Table -1.**

It was observed that compounds having fluoro and chloro group (**4b**, **4c** and **5b**) exhibited better insecticidal activity (KD value is 2-5 min.) in comparison to standard drug (KD value is 5-7 min.). The rest of the compounds have significant to moderate activity (KD value is 5-9 min).Form the above studies; it is clear that some of these derivatives can be used to develop new insecticides.

Table-1 Insecticidal activity of the synthesized compounds against *Periplaneta americana* (KD values in min)

Compound	Time (min)	
	1% (Conc.)	2% (Conc.)
3a	6	5
3b	7	5
3c	6	5
4a	7	5
4b	5	2
4c	5	2
5a	6	5
5b	5	2
5c	7	5
5d	9	6
5e	7	6
Cypermethrin	7	5

CONCLUSION :

The present investigation of the reaction 3-[2-oxo-2-(2-thienyl)ethylidene]indol-2(1H)-ones (**1**) with 2-hydrazinobenzimidazole**(2)** was carried out in different media and solvents and found that 2,2,2-trifluoroethanol is good solvent to achieve spiro[indole-3,3'-pyrazole]-2(1*H*)-ones in excellent yield.The synthesized compounds (**3a-c , 4a-c and 5a-e**) were screened for their insecticidal activity against *Periplanata americana* using Cypermethrin as standard and the data revealed that some compounds were even more active than the standard and could act as potential insecticidal agents.

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