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RESEARCH ARTICLE

A CONCISE OVERVIEW ON HETEROCYCLIC COMPOUNDS EXHIBITING PESTICIDAL ACTIVITIES

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Abstract

Heterocyclic compounds are numerous and diverse group of organic compounds. Heterocycles are abundantly found in nature and express various physiological properties. Heterocycles are intricately linked to all aspects of life. There are many heterocyclic compounds currently known, and the number is constantly rising owing to extensive synthetic development and their applications. Heterocyclic compounds are used significantly in a number of areas, including biochemistry and medicinal chemistry, and some others. They are predominantly synthesized in agrochemical and pharmaceutical industries due to their potential biological activities. This review article focuses on recently synthesized heterocyclic compounds and their different pesticidal activities such as antifungal, antibacterial, antiviral, nematocidal, insecticidal, acaricidal, and herbicidal.

Introduction:-

Heterocyclic compounds, especially the 5 & 6 membered compounds of one, two or three heteroatoms in their nucleus, play an important role in the metabolism of all living organisms. However, the compounds existing with 7 or more membered heterocyclic compounds are equally effective. Heterocyclic compounds may be fused or independent heterocyclic structures, as they exist in genetic material like purine and pyrimidine. Most drugs fall under the category of heterocyclics and possess physiological role in living organism.

Pesticides are effective resources in agriculture for protecting crops, increasing yield, and improving efficiency. Chemical pesticides have shown their value by boosting worldwide agricultural production, decreasing endemic illnesses, insect-borne, and protecting forests, plantations, houses, harvested wood products, and fibre. The necessity to boost global food production in order to feed the world's rapidly increasing population is widely understood. Effective pest management is one of the methods for increasing agricultural output since pest infestation accounts for more than 45 percent of yearly food production. Crop loss is much worse in tropical nations because the high temperatures and humidity encourage pests to multiply quickly. In order to fight pests and vector-borne illnesses, a broad range of pesticides must be applied to agricultural plants in the tropics.

According to many review of the literature, a variety of heterocyclic compounds with a condensed ring structure exhibit a wide range of physiological activities in different ways. Several antifungal [1,2], antibacterial [3,4], and

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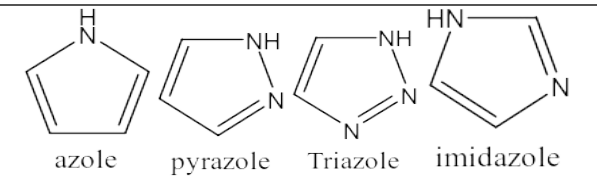
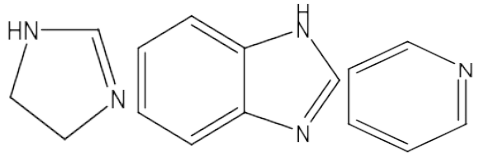
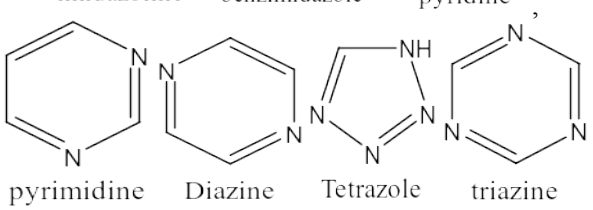
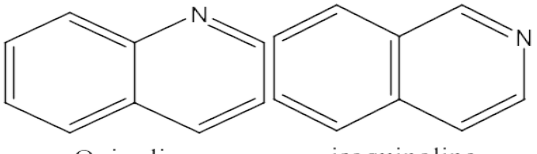
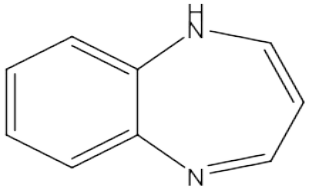
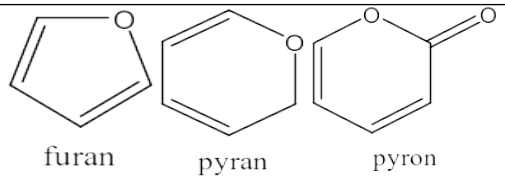
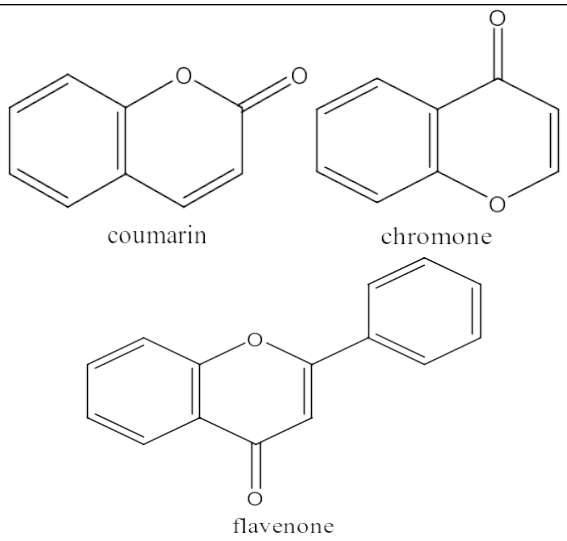
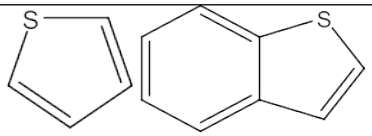
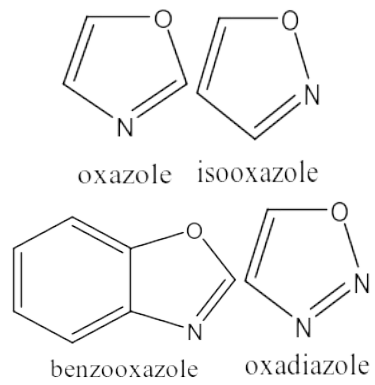
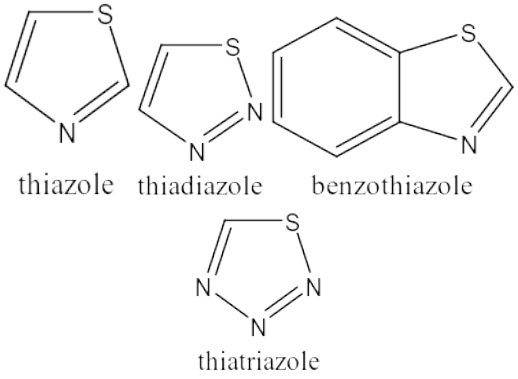
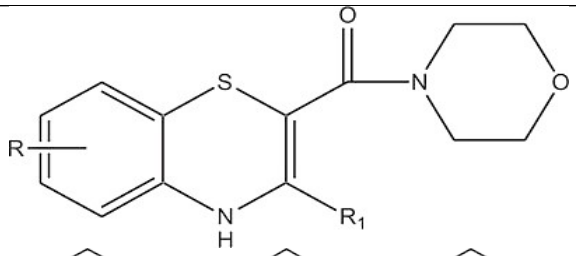
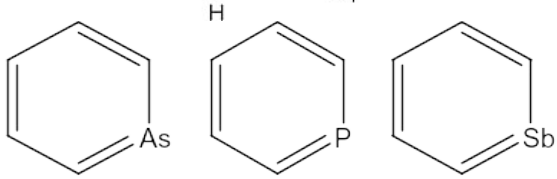
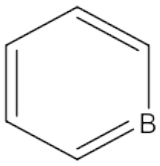
herbicidal [5,6] properties have been shown for condensed N-benzylidene and triazolo-pyrimidines derivatives. The different pesticidal activities are shown in figure 1.

Types of heterocyclic compounds : It is hard to mention all heterocyclic compounds due to their very large number, however a general classification of heterocyclic compounds on the basis of types ofhetero atom present in the ring is given in Table:1.

Table-1:- A general classification of heterocyclic compounds.

Sn.	Heterocyclic compounds	Types	Pesticidal activity
1.	**Nitrogen Heterocyclics**	 azole pyrazole Triazole imidazole  imidazoline benzimidazole pyridine  pyrimidine Diazine Tetrazole triazine  Quinoline isoquinoline  1,5-benzodiazepine	They show specially insecticidal, herbicidal, fungicidal activity. Most of drugs belongs to these types.
2.	**Oxygen Heterocyclics**	 furan pyran pyron	Shows potential herbicidal, antifungal, antibacterial activity

			
3.	**Sulphur Heterocycles**		Shows herbicidal, insecticidal, fungicidal and other pesticidal activity given in Fig.1
4.	**Nitrogen and oxygen heterocycles**		Shows herbicidalInsecticidal andother biological activity
5.	**Sulphur and nitrogen heterocycles**		They are good insecticides, herbicides and most of agrochemical belongs to this category.

6.	**Miscellaneous**	  arsabenzene phosphabenzene stibabenzene  borabenzene **and derivatives of these and other heterocyclics containing 3, 4, 5, 6, 7, 8-member ring with one hetero atom or more than one heteroatom**	Shows all the pesticidal activity.

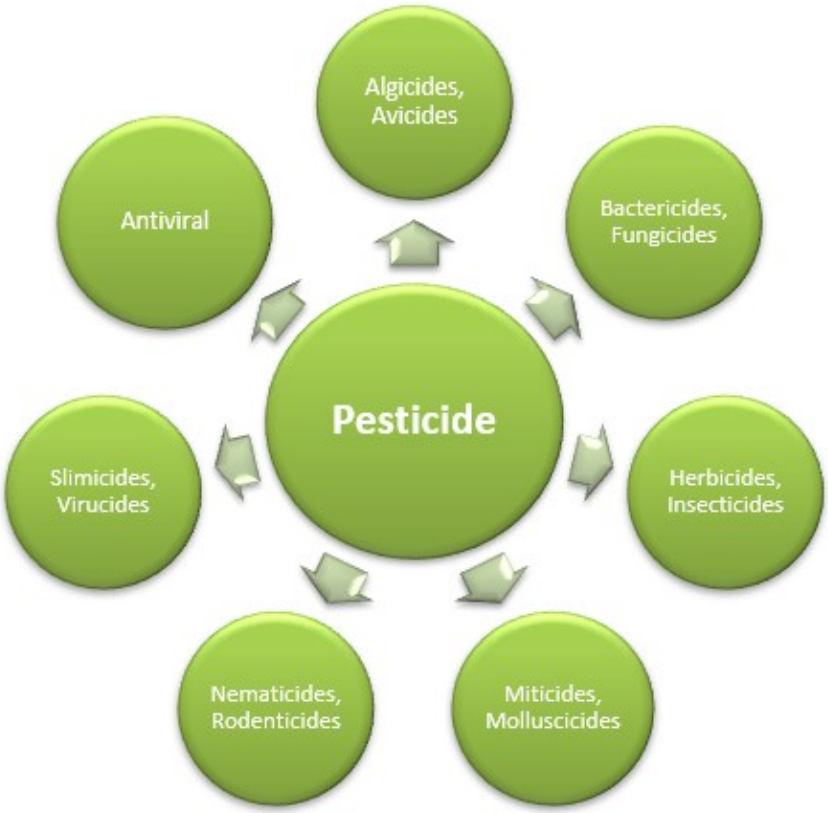


Figure-1:- Types of pesticidal property.

Antifungal activity

Lukowska-Chojnacka et al. (2016) [7] utilized phenylsulfonyl moiety and prepared4new derivatives of 2,5-disubstituted tetrazole (Figure 2). The synthesized derivatives showed excellent in-vitro antifungal activity towards*A. niger, F. oxysporum, F. sambucinum,* and *C. coccodes*, according to bioassay findings. Only *C. coccodes*did not showed much inhibition againstall the target derivatives tested. However, all the target derivatives worked against *C. albicans* at the same level and showed significant cell development inhibition (97–99 percent) at doses oscillatingbetween 0.03 to 15 g/mL, which remainedless as compared to amphotericin B.

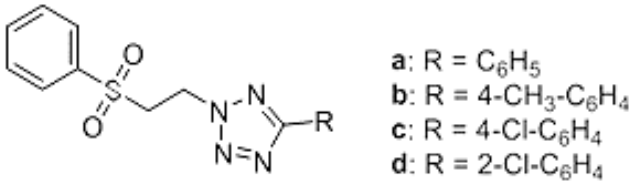


Figure-2:- Compound 1.

Xu et al. (2017) [8] used "[1,2,4] triazolo[4,3-a] pyridine" moiety to synthesizea variety of new sulfone compounds and tested them towards,*H.maydi,R.cerealis,R.solani,* and*F.grameinearum.* The bioassay findings showed that "8-chloro-3-((2,6-difluorobenzyl)sulfonyl)-[1,2,4]triazolo[4,3-a]pyridine" (compound 2) had excellent in-vitro antifungal activity towards*H. maydis* and *R. erealis* at (50 g/ml), with reserverates of 76.4 and 78.6 percent, respectively.

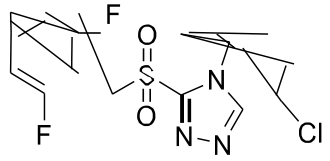


Figure-3:- Compound 2

Molnar et al. (2017) [9] created a variety of derivatives of dipicolinic acid (Figure 4), some of which exhibited antifungal property towards*Aspergillus ochraceus, Aspergillus flavus, Fusarium verticilioides*, and *Fusarium graminearum* fungal species.

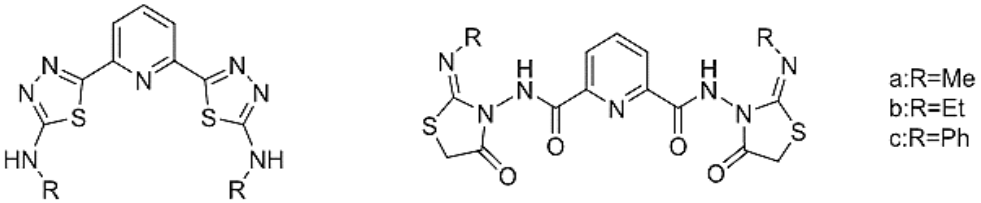


Figure-4:- Compound 3

Chitra et al. (2017) [10] produced biopolymeric hydrogels (Compound 4) with indole 3-acetic acid, which showed antifungal efficacy towards *Rhizopus oryzae*, *Aspergillus fumigates*, and *Candida albicans* at various doses utilizing Dimethyl Sulfoxide as a negative control and ketoconazole as a positive control.

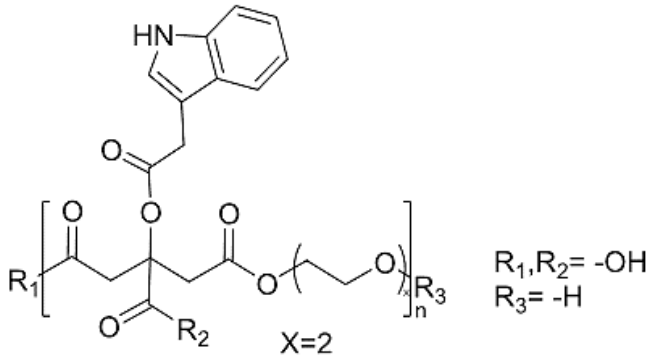


Figure-5:- Compound 4

Muslim RF et al. (2018) [11] created novel disubstituted 1,3-oxazepine-5-one heterocyclic compounds (Figure 6). Azomethine compounds (N1-N5) were created by reacting aromatic aldehydes with primary aromatic amines in 100% ethanol using glacial acetic acid as a catalyst. In general, N9 is the best derivative, with a substantially ($p<0.01$) greater effect on Candida sp. growth inhibition.

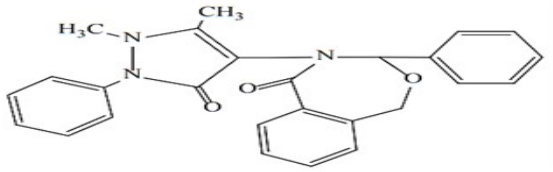


Figure-6:- Compound

Hua et al. (2020) [12] produced a variety of new aromatic amide derivatives with a sulfone substructure. The target compounds have lower antifungal activity than fluopyram towards *A. kikuchiana Tanaka, B. cinerea, C. capsica, C. circumscissaSacc., G. zeae, P. piricola, P. vexans and R. solani,* according to bioassay findings.

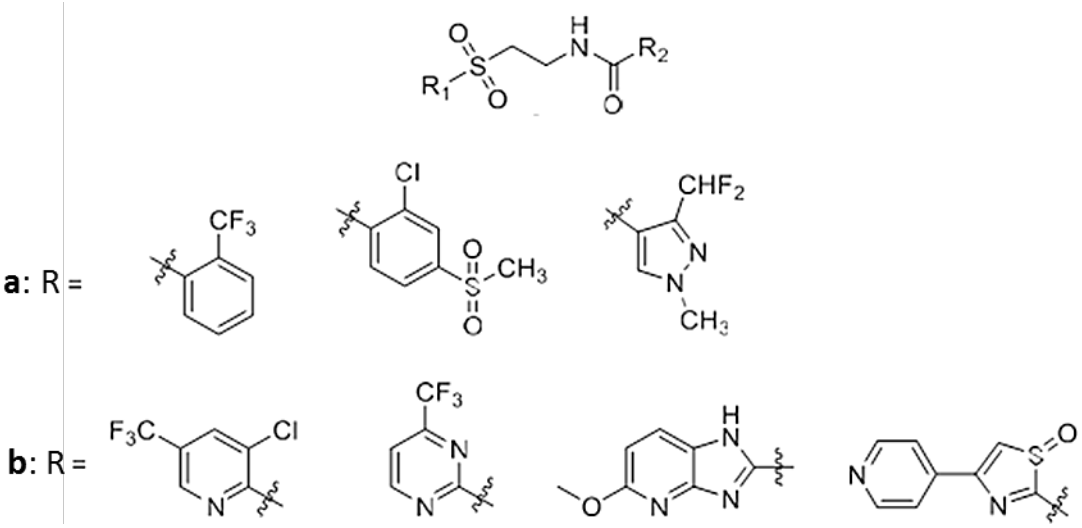


Figure-7:-Compound 6

Sol Ballari et al. (2019) [13] synthesized many new derivatives of 2-(benzylsulfonyl)benzothiazole (Figure 8). The derivatives obtained were subjected to bioassays and the findings revealed that several derivatives had good antifungal activity towards *A. niger, A. ustus, A. terreus, A. fumigatus, B. cinerea,* and *F. oxysporum*. Compound (7a) demonstrated the best antifungal activities towards *A. terreus* and *B. cinerea*, with EC50 values of 0.3 and 4 M, respectively, when compared to captan, whereas compound (k) demonstrated healthy antifungal activities towards*A ustus ,A. niger,* and *A. fumigatus*, in EC50 standards of 14, 6.3, and 2.3 μM.

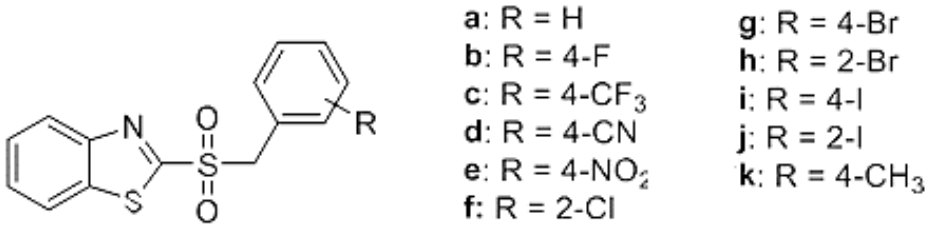
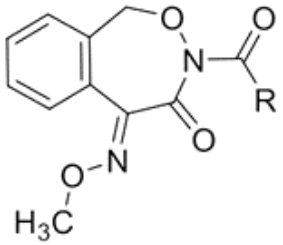


Figure-8:-Compound 7

YandD et al. (2021) [14] synthesizedthe "(E)-3-acyl-5-(methoxyimino)-1,5- dihydrobenzo[e][1,2]oxazepin-4(3H)-one"(compound 8) analogues and thoroughly investigated the antifungal activities. 5r was shown to be very effective towards *B. cinerea and S. sclerotiorum*."(E)-3-(4-(dimethylamino)benzoyl)-5- (methoxyimino)-1,5-dihydrobenzo[e] [1,2]oxazepin4(3H)-one" showed excellent antifungal activity towards S. sclerotiorum and B. cinerea.



where,R=4-N, $N(CH_3)_2$-PH

Figure-9:- Compound 8

Antibacterial Activity

Li et al. (2014) [15] produced a variety of derivatives "2,5-disubstituted-1,3,4-thiadiazole/oxadiazole"(Figure 10). "2-(Methyl sulfonyl)-5-(4-fluorobenzyl)-1,3,4-oxadiazole" had the greatest in-vitro antibacterial activity towardsXoo, Xac, &Xoc, with EC-50 standards of 1.23, 7.14, and 1.07 g/mL, respectively. The EC50 values were found to be better thanbismerthiazol,thiodia, bismerthiazol and kocide 3000. However, in-vivo antibacterial activity testing in greenhouse settings revealed that "2-(Methyl sulfonyl)-5-(4-fluorobenzyl)-1,3,4-oxadiazole" had superior control of rice bacterial leaf blight of rice bismerthiazoland thiodiazole copper. Furthermore, "2-(Methyl sulfonyl)-5-(4-fluorobenzyl)-1,3,4-oxadiazole" showed best potential to decrease the illness of "citrus canker" in fruits and leaves in a field trial towards citrus canker in 2 different locations when compared to a control and the profitable bactericidesthiodiazole copper and kocide 3000.

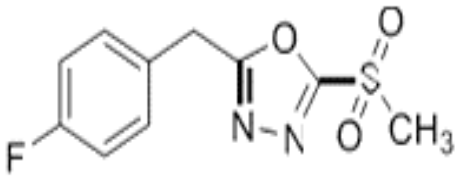


Figure-10:- Compound 9

Wu et al. (2016) [16] utilized 1,3,4- thiadiazole/oxadiazole moiety to synthesize variouspurine derivatives (figure 11) and used the turbidimeter test to assess their in-vitro antibacterial activity towards *Xoo*and*R. solanacearum*. The derivatives showed excellent inhibitory activities towards*R. solanacearum* and*Xoo*in antibacterial bioassays. These results were improved as related withbismerthiazol&thiodiazole copper.

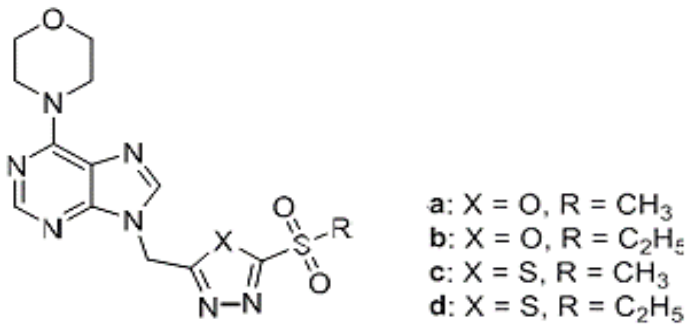


Figure-11:- Compound 10.

Pyridinium-tailored "2,5-disubstituted-1,3,4-oxadiazole"sulfoxide/thioether/sulfone derivatives (Figure 12) wereproduced by Wang *etal.* (2016) [17]. Most of the derivatives had greater inhibitory activities towards*R.solanacearum*Xac,Xoo.as compared withbismerthiazole andthiodiazole copper, according to bioassays.

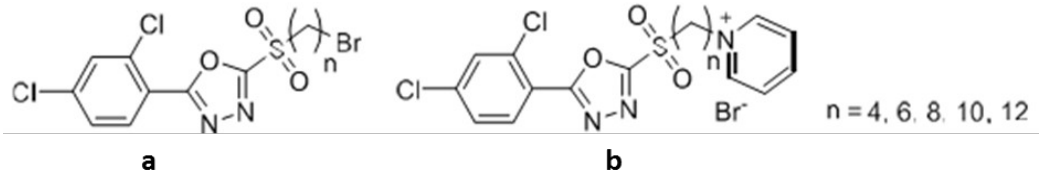


Figure-12:- Compound 11.

Zheng et al. (2017) [18] produced a variety of new derivatives of "2-sulfone-5-pyrazolyl-1,3,4-oxadiazole" (Figure 13). The findings of bioassays designated that several areas of chemicals have significant anti-Xoo action. Compound (12 c) has the greatest antibacterial action towards Xoo (EC50 = 16.6 g/mL) among the test compounds, outperformingbismerthazol and thiodiazolecopper.

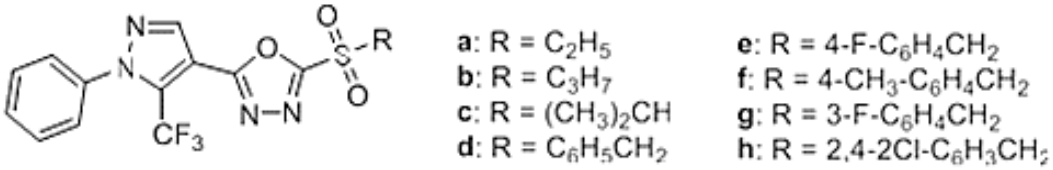


Figure-13:- Compound 12.

Similarly, Su et al. [19] created a variety of original sulfone derivative by inserting the aryloxymethyl moiety into the "1,3,4-oxadiazole/thiadiazole" sulfone scaffold.

The findings of antimicrobial activity showed that several of the derivatives had much greater antibacterial activity than thiadiazole copper and bismerthiazol towards *R. solanacearum*, Xac, and Xoo.

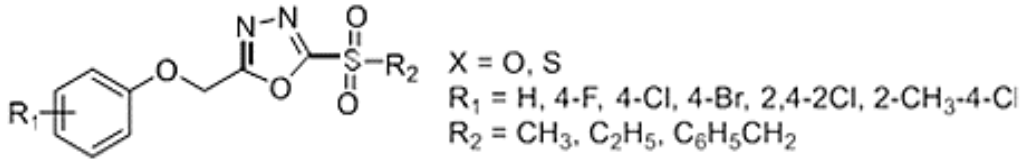
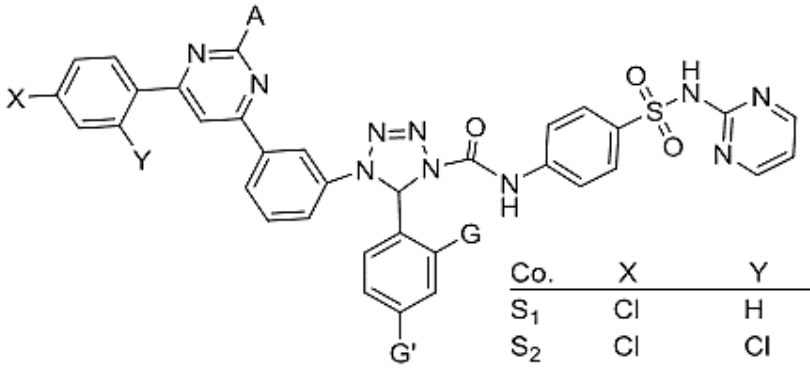


Figure-14:- Compound 13.

Abbass and Zimam [20] developed novel pyramidine and "1,2,3,4-tetrazole"derivatives based on sulfadiazine (Figure 15) and tested them on 2 kinds of bacteria: *Porphyromonasgingivalis* (Gram-negative) or *Streptococcus spp.* (Gram-positive).



Co.	X	Y	A	G	G'
S_1	Cl	H	OH	$N(CH_3)_2$	H
S_2	Cl	Cl	SH	Br	H
S_3	$N(CH_3)_2$	H	SH	Cl	Cl
S_4	OCH_3	OH	OH	Cl	H
S_5	Br	H	NH_2	OH	H

Figure-15:- Compound 14.

Iqbal et al. (2017) [21] produced derivatives of "N-substituted acetamide of azinane-bearing 1,3,4-oxadiazole" and tested their anti-bacterial efficacy towards 5 bacterial species (*Salmonella typhi, Bacillus subtilis* ,S aureus, *Salmonella typhi, Pseudomonas aeruginosa and Escherichia coli*).

All the produced compounds were mild inhibitors, although Gram-negative bacterial strains were more active except for *S. aureus*, 1,3,4-oxadiazole was the most effective inhibitor of growth of bacteria.

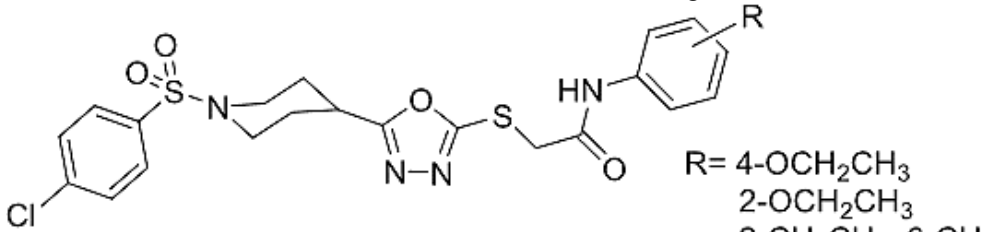


Figure-16:- Compound 15.

Li et al. (2018) [22] synthesized several novel sulfone compounds with a "1,3,4-oxadiazole moiety" and tested their antibacterial activity in-vitro towardsXac&Xoo. When compared to thiodiazole copper and bismerthiazol, the antibacterial bioassay findings indicated that "2-(methylsulfonyl)-5-((4-fluorophenyl)sulfonyl)methyl)-1,3,4-oxadiazole" had outstanding bioactivities against Xac&Xoo, values of EC50 1.98 and 0.17 g/mL, singly. Meanwhile, greenhouse experiments revealed that "2-(methylsulfonyl)-5-((4-fluorophenyl)sulfonyl)methyl)-1,3,4-oxadiazole" reduced bacterial leaf blight ofrice extracompetently than bismerthiazol and thiadiazol copper.

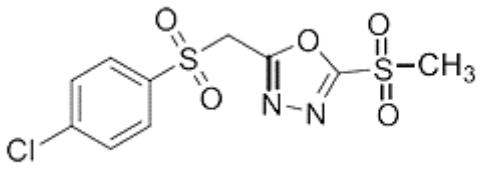


Figure-17:- Compound 16.

Deng etal. (2017) [23] have created variety in novel tetracycline offshoots. "1,7-trifluoromethyl-8-pyrrolidinyltetracyclines", a wide-range antibacterial with improved *P. aeruginosa*action.

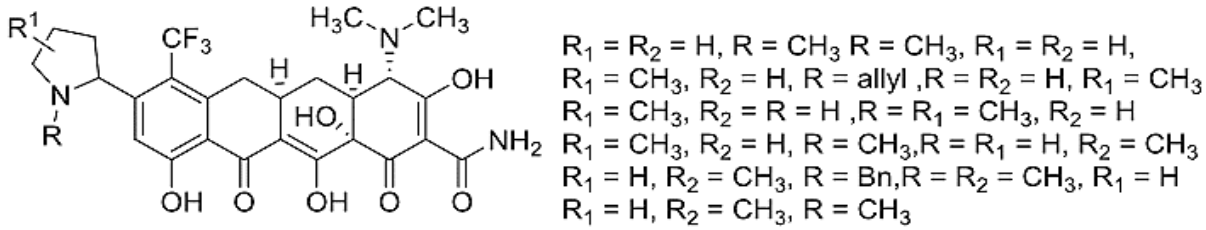


Figure-18:- Compound 17.

Zhang et al. (2019) [24] utilized 1,3,4-thiadiazole moiety and published a series of sulfone derivatives. When compared to bismerthiazol and thiodiazole copper, bioassay findings presentedthat several of the complexpresenteddecent antibacterial activity towards Xac, R. solanacearum and Xoo. Compound (18 a) in particular had high efficacy towards Xoo in vitro, surpassing bismerthiazole and thiodiazole copper. However, in vivo antibacterial activity findings revealed that compound (18 a) showed almost comparable protective and curative effect towards bacterial leaf blight of rice compared tobismerthiozol and thiodiazole copper.

Chen et al. (2019) [25] produced a variety of novel sulfone derivatives combining amide and "1,3,4-thiadiazole". Antibacterial activity tests indicated that compound (18 c) had better antibacterial activity against Xac,*R. solanacearum*, and Xoo, compared to thiodiazole copper, bismerthiazol, and fluopyram. The control effectiveness of compound (18 c) towards bacterial leaf blight of rice at 200 mg/L in greenhouse circumstances showed that, when compared to thiodiazole copper, bismerthiazol, and fluopyram, compound (18 c) was more efficient in fallingbacterial leaf blight of rice.

Wang etal. (2019) [26] also utilized 1,3,4-oxadiazole moiety to synthesize a variety of new sulfone derivatives and found that compound (18 b) had higher antibacterial activity towards Xoc&Xoo in vitro and in vivo thanbismerthiozol and thiodiazole copper.

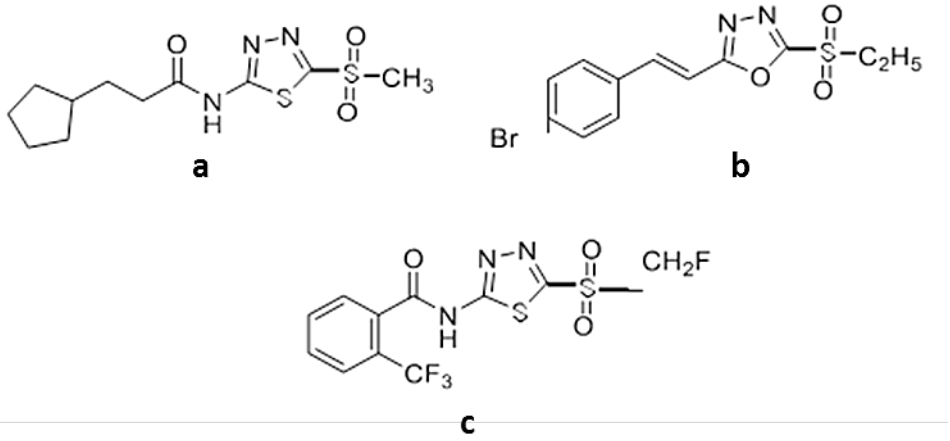


Figure-19:- Compound 18 (a,b,c).

Chen et al. (2020) [27] used "1,3,4-oxadiazole" moiety and developed a series of new sulfone compounds and performed antibacterial assay. Thebio-assay findings exposed that all of the derivatives had good in-vitro antibacterial activity towards Xoo. Compound (19 a) had superior antibacterial activity towards Xoo as compared tobismerthiazole and thiodiazole copper.

Xiang et al. [28] used 1,3,4-dichloroisothiazolamide moiety and created a series of "1,3,4-oxadiazole sulfone"offshoots. Compound (19 c) had outstanding in-vitro antibacterial activity towards"Xoo and Xoc", values of EC50 with 2.21 and 0.79 g/mL, which were found to be better than bismerthiazol,isotianil, and thiodiazole copperaccording to bioassay findings. Compound (c) had a higher control efficiency toward rice bacterial leaf blight in green-house circumstances at 200 mg/l than thiodiazole copper, isotianil, and bismerthiazol, with protection and

curative activities of 41.06 percent and 43.99 percent, respectively, compared to isotianil,bimerthiazol and thiodiazole copper.

Li et al. (2020) [29] established novel class of sulfone compounds with a sulfonohydrazide moiety. The antibacterial activities of compound (19 b) against Xac&Xoo were the best, with EC50 values of 36 and 25 g/mL, which were found to be better compared with bismerthiazoland thiadiazol copper.

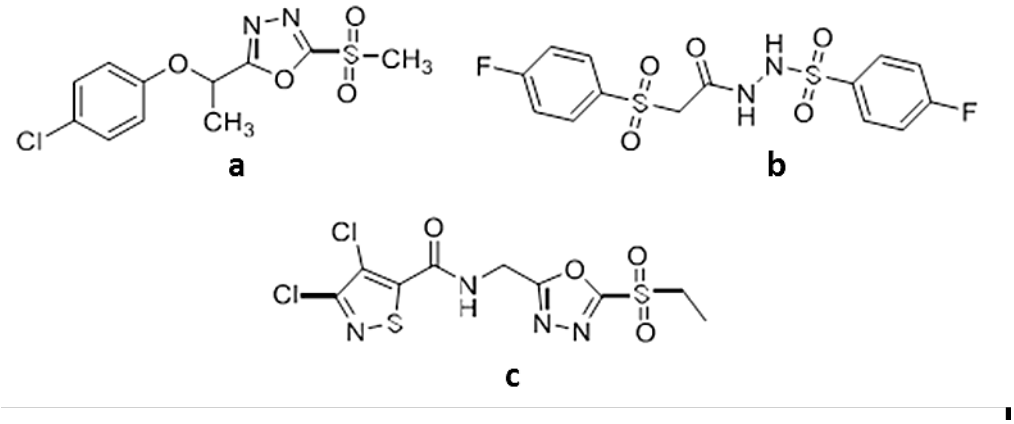


Figure 20:- Compound 19 (a, b, c).

Antiviral Activity

Viral diseases, such as the hepatitis, herpes,influenza, common cold,HIV,gastroenteritis, chickenpox, and the Ebola virus, are among the most prevalent infections throughout the world. Antiviral treatment is crucial in preventing viral infections from spreading.

Xu et al. (2013) [30] used "1,3,4- oxadiazole/thiadiazole"piece to produce anoriginal class of sulfone compounds (Figure 21). When compared to ningnanmycin, antiviral activity findings indicated that several of the derivatives had moderate to excellent antiviral efficacy towards TMV.

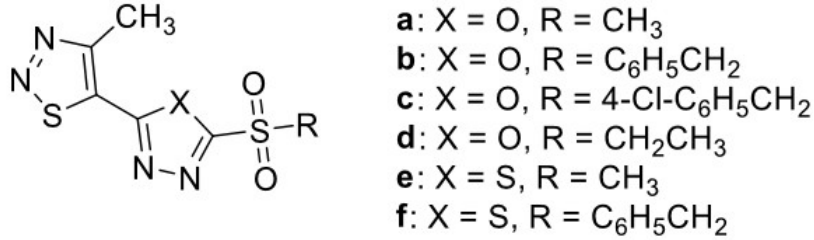


Figure 21:- Compound 20.

Wu et al. (2015) [31] synthesized a variety of 1,3,4-thiadiazole and pyrazol containing sulfone derivatives. (Figure22). When compared to ningnanmycin, antiviral action findings presented that the synthesized compounds showed excellent antiviral efficacy compared to TMV.

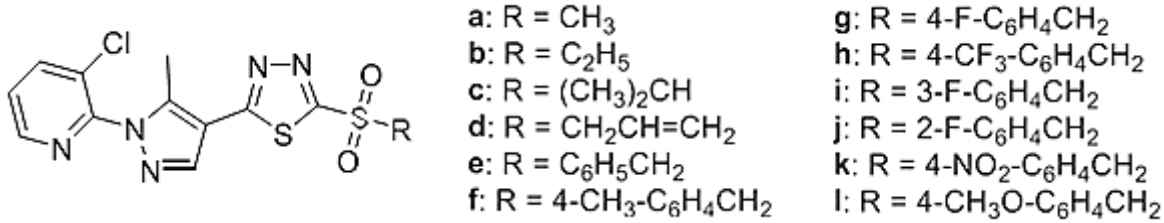


Figure 22:- Compound 21.

Nematocidal activity /Insecticidal activity /Acaricidal activity

Wang et al. (2014) [32] produced four new pyrazole containing moiety sulfone derivatives (Figure 23). The target compounds have lesser larvicidal efficacy towards *M. separata* than chlorantraniliprole, according to bioassay findings.

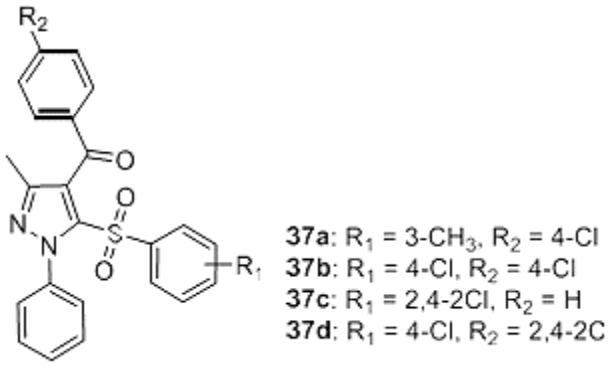


Figure 23:- Compound 22.

Yu et al. (2016) [33] used "2,4-diphenyl-1,3-oxazolines"fraction to synthesizeor test a variety of new sulfone derivatives for insecticidal and acaricidalactivity in 2016. The bioassay findings revealed that compound(23 a) had even greater acaricidal action towards*T. cinnabarinus eggs*as compared toetaxazole. Song's group [34] used 1,3,4-oxadiazole/thiadiazolefraction to synthesize a sequence of sulfone offshoots. The bioassay findings indicated that compound(23 b) had outstanding action of nematicidal (100 percent) towards C. elegans at 48 & 72 hours.

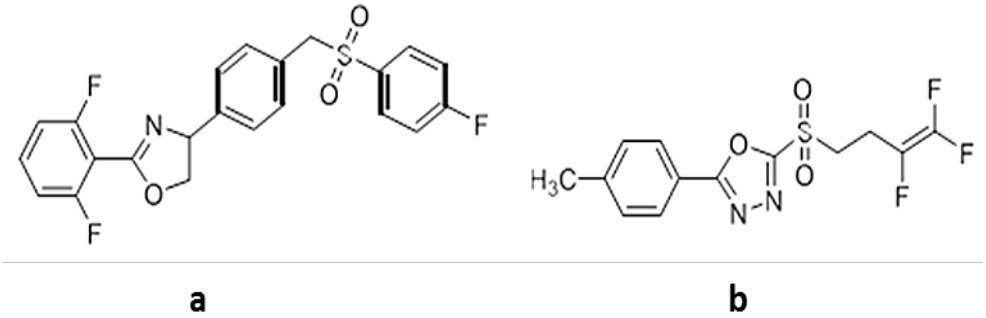


Figure 24:- Compound (23 a, b).

Xu et al. (2017) [8] discovered that compound 24 (Figure 25) had excellent insecticidal activity towards *H. armigera* (> 90%) and *P. xylostella* (> 95%) at (500 μg/ml))

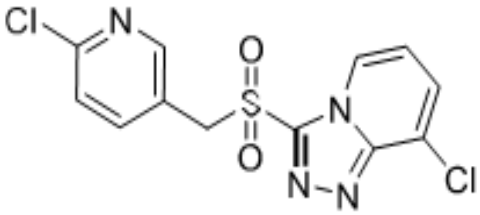


Figure 25:- Compound 24.

Li et al. (2019) [35] used anthranilic diamide moiety to synthesize and test a sequence of new sulfone offshoots for insecticidal activity towards *P. xylostella* and *M. separata*. Bioassay findings revealed that compound 25 (Figure 26) had higher insecticidal effects towards*P. xylostella* (100%) and *M. separata* (100%) than chlorantraniliprole at 1-200 mg/L.

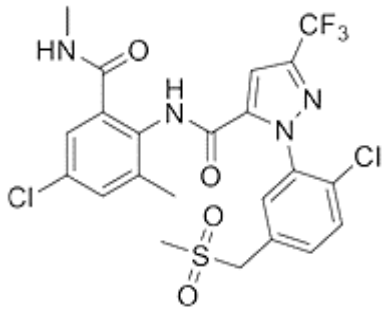


Figure 26:- Compound 25.

Hua et al. (2020) [36] discovered that compound 26 (Figure 27) had admirable nematocidal activity towards *M. incognita*, with a deathamount greater than 80% when compared to fluopyram.

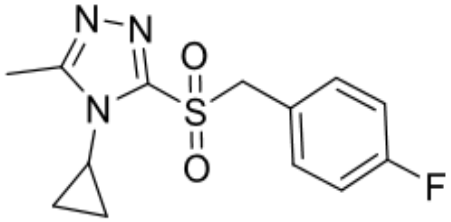


Figure 27:-Compound 26

Herbicidal activity

Min et al. (2014) [37] used 1,2,4-triazole and announced a novel sulfone derivative (Figure 25). The bioassay findings indicated that compound 27 inhibited root more effectively (73%) and had less action towards KARI (35%) and *E. crusgalli*(28%) as compared tothe"cyclopropane-1,1-dicarboxylic acid" at 100 g/ml.

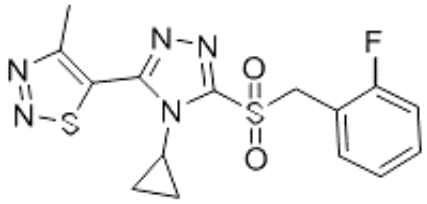


Figure28:- Compound 27

Wang et al. [38] produced fluorin-containing "2-(substituted phenoxybutyryloxy)alkyl-5,5-dimethyl-1,3,2-dioxaphosphinan-2-one" and "a-[(substituted phenoxybutyryloxy or valeryoxy)]alkylphosphonates". In a greenhouse, these chemicals demonstrated herbicidal activity towards a variety of weed species.

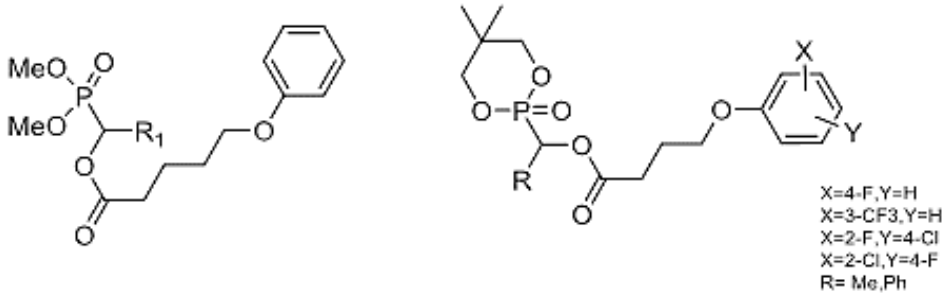


Figure 29:-Compound 28

Yang and Tian (2019) [39] used aryl carboxylamide moiety and created 4 sulfone derivatives. At 1000 g/ha, herbicidal activity findings revealed that compound 28 (Figure 29) exhibited in high inhibitory action (77.74 percent) towards "*E. crusgalli"*. Similarly, Min et al. [37] demonstrated , at 100 or 10 g/ml, compound 29 has excellent action towards *B. campestris*, but has poor activity towards KARI and *E. crusgalli*.

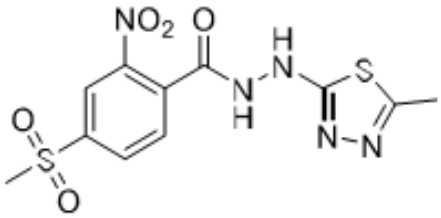


Figure30:- Compound 29

Conclusion:-

Heterocyclic compounds are the complex group in organic chemistry. These compounds are essential in a number of ways. Pharmacology and biochemistry are the two main fields that collectively contribute to the holistic efficacious vitality of the compounds having activity against pests. Synthetic organic chemistry finds huge application that requisitely meet the needs of modern society and mankind by synthesizing new biologically active heterocyclic compounds. Most importantly they safeguard crop health by killing the harmful pest and plants that restrict its growth. Besides, heterocyclics are also useful in treatment of animals and human as a therapeutical agent. Heterocyclic compounds show good herbicidal, insecticidal, antifungal, nematocidal, antibacterial and antimicrobial activities. The present review is an attempt to briefly compile the heterocyclic compounds for their pesticidal properties.

Table-2:- Pesticidal properties of different compounds**.**

Sn.	Compounds	Pesticidal property	References
1	2,5-disubstituted tetrazole derivatives	Antifungal activity	[7]
2	8-chloro-3-((2,6-difluorobenzyl)sulfonyl)-[1,2,4]triazolo[4,3-a]pyridine	Antifungal activity	[8]
3	disubstituted 1,3-oxazepine-5-one derivatives	Antifungal activity	[11]
4	Aromatic amide derivatives	Antifungal activity	[12]
5	2-(benzylsulfonyl)benzothiazole	Antifungal activity	[13]
6	(E)-3-acyl-5-(methoxyimino)-1,5-dihydrobenzo[e][1,2]oxazepin-4(3H)-one	Antifungal activity	[14]
7	2,5-disubstituted-1,3,4- thiadiazole/oxadiazole	Antibacterial activity	[15]
8	4-(9-((5-substituted-1,3,4-oxadiazole/ thiadiazole-2-yl)methyl)-9H-purin-6-yl)-morpholine	Antibacterial activity	[16]
9	2,5-substituted-1,3,4-oxadiazole sulfoxide/thioether/sulfone derivatives	Antibacterial activity	[17]
10	2-sulfone-5-pyrazolyl-1,3,4-oxadiazole derivatives	Antibacterial activity	[18]
11	1,3,4-oxadiazole/thiadiazole sulfones	Antibacterial activity	[19]
12	1,2,3,4-tetrazole derivatives	Antibacterial activity	[20]
13	N-substituted acetamide of azinane-bearing 1,3,4-oxadiazole derivatives	Antibacterial activity	[21]
14	2-(methylsulfonyl)-5-((4-fluorophenyl)sulfonyl)methyl)-1,3,4-oxadiazole	Antibacterial activity	[22]
15	1,7-trifluoromethyl-8-pyrrolidinyltetracyclines	Antibacterial activity	[23]
16	1,3,4-oxadiazole sulfone derivatives	Antibacterial activity	[28]
17	thioether/sulfone compounds containing 1,3,4-oxadiazole/1,3,4-thiadiazole	Antiviral activity	[30]
18	N-phenylpyrazolyl aryl methanones derivatives	Larvicidal activity	[32]

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