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1,3,4-OXADIAZOLE AND ITS POTENCY: A REVIEW

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Keywords:

1,3,4oxadiazole, Biological activity, Antimicrobial, Anti tubercular, Analgesic, Anti-inflammatory, Anticonvulsant, Anti HIV, Antipyretic, Anti-alzheimer

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ABSTRACT: Heterocyclic compounds represent the important structural key in pharmaceutical medicinal chemistry. In literature, five-membered heterocycles are reported to be a core moiety of various pharmaceutical drugs. Oxadiazole or furadiazole is a five-membered heterocyclic nucleus and is considered to be derived from furan by replacement of two methane (-CH=) groups by pyridine type nitrogen. Oxadiazole is a versatile lead compound for designing potent bioactive agents. 1, 3, 4-oxadiazole having verities of potential biological activities can be synthesized by various methods. Hence, nowadays, researchers have developed innovative methods for the synthesis of 1, 3, 4-oxadiazole derivatives and their medicinal applications. The activities include anticancer, antimicrobial, anti-inflammatory, anti-HIV, anti-tubercular, anti-diabetic, antifungal, *etc*. In this review article, we have summarized various methods for synthesis of derivatives of 1, 3, 4 – oxadiazole nucleus and evaluation of various biological activities. The information in the present article may be useful to many researchers, which leads to the exploration of new therapeutic species for society.

INTRODUCTION: The heterocyclic compounds have always been a fascinating part of a study in the field of chemistry. Nitrogen, oxygen & sulphur are some heteroatoms present in the rings replacing carbon. Substitutions on the heterocyclic drugs give them more potency and diverse functionalization. The important compounds present in vitamin- B complex, dyes, enzymes, antibiotics, alkaloids, amino acids and drugs are heterocyclic compounds which are having therapeutic uses.

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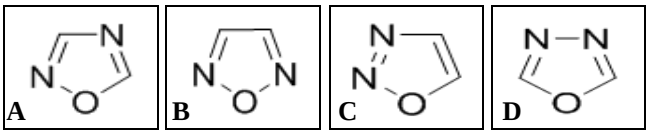
The five-membered oxadiazole nucleus present in heterocyclic compounds is majorly responsible for the diversified useful biological effects. When two methine (-CH=) groups present in the furan ring are replaced by two pyridine type nitrogen (-N=) then oxadiazole is derived with the general formula of $C_2H_2ON_2$, this reduces the aromaticity of the ring (oxadiazole) to some extent that they now reflect the characteristics of a conjugated diene. The electrophilic substitution reactions are not possible in oxadiazole because of the low density of electrons on the carbon atom, which causes the electron withdrawal effect of pyridine type nitrogen when any electron releasing group was added to it.

The oxadiazole ring is found to be resistant to nucleophilic substitutions. Whereas the halogen-substituted oxadiazole can undergo these sub-

stitutions by replacing halogen atom by nucleophiles. Four isomers of oxadiazole are present.



A. 1, 2, 4-Oxadiazole, B. 1, 2, 5-Oxadiazole, C. 1, 2, 3-Oxadiazole, D. 1, 3, 4-Oxadiazole

1,2,4-oxadiazole, 1,2,5-oxadiazole, and 1,3,4-oxadiazole are known, but the 1,2,3-isomer is quite unstable and reverts in the form of diazoketone tautomer. The stable oxadiazoles appear in a many pharmaceutical drugs which include raltegravir, fasiplon, butalamine, oxolamine, pleconaril and Nesapidil. Oxadiazole have occupied a unique place in the field of medicinal chemistry due to its wide range of activities like antimicrobial, anti-inflammatory, anti-fungal, antitubercular, anti-convulsant, anthelmintic, herbicidal, antioxidant, analgesic, anti-tumour, and anti-hepatitis B viral activities.

Biological Activities: It is an important, challenging task for medicinal chemists to develop new anti-microbial, anti-inflammatory, analgesic, antitumor, anti-convulsant, anthelmintic, herbicidal, antimycobacterial and anti-oxidant agents**.** There are two basic approaches for the development of new drugs:

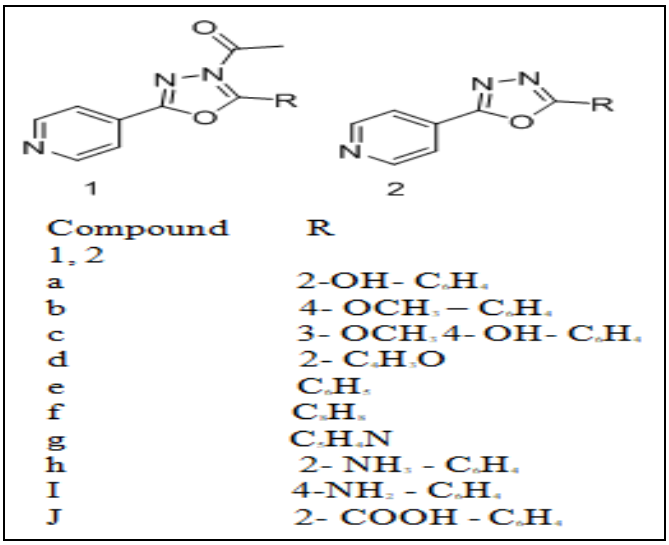
(a) Synthesis of analogous and their modifications as well as derivatization gives novel substituted compounds for better and improved treatment and

(b) Searching and synthesis of novel compounds, that the bacteria and diseases has never been presented before. For this purpose, substituted 1, 3, 4-oxadiazoles are already being used as potent anti-microbial, anti-inflammatory, analgesic, anti-tumor and anti-convulsant, documented as well as patented.

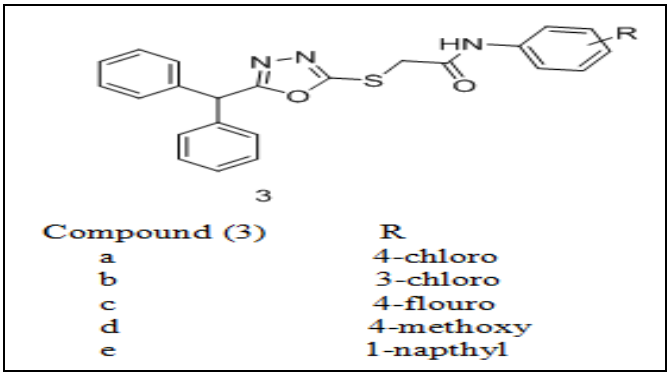
Biological Activity of 1, 3, 4-oxadiazole:

Analgesic and Anti-inflammatory Activity: The novel mercapto substituted 1, 3, 4-oxadiazole bears good anti-inflammatory activity and if secondary amines are added to this scaffold, then the activity increases [1].

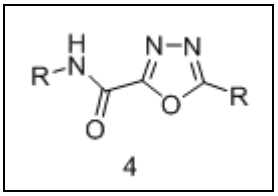
Dhansay Dewangan *et al.*, (2010) synthesized 2, 5-disubstituted 1, 3, 4-Oxadiazole derivatives 1 and 2, newly synthesized compounds were investigated for their analgesic activity by Acetic acid-induced writhing method using Swiss albino mice (25-35g) and anti-inflammatory activity by carrageenan-induced rat paw edema and were determined according to mercury displacement method by using plethysmograph on adult albino rats (150-180g). So compound 1b, 2f and 2j were shown significant analgesic activity, whereas compound 1c, 2g and 2j were shows good anti-inflammatory activity [2].



Mohammad Amir *et al.*, (2011), synthesized 2-[(5diphenylmethyl-1,3,4-oxadiazole-2-yl)sulfanyl]-N(substitutedphenyl)-acetamides 3a-e, newly synthesized compounds were investigated for their anti-inflammatory effect by carrageenan-induced paw edema model using wistar rats (180-200g), analgesic activities of the compounds were studied by tail immersion method using albino mice (25-30g). The compounds 3a, 3b, and 3c showed significant anti-inflammatory activity [3].



Singh AK, *et al.*, (2013) have synthesized a series of 1, 3, 4- oxadiazole derivatives and evaluated for anti-inflammatory activity [4].



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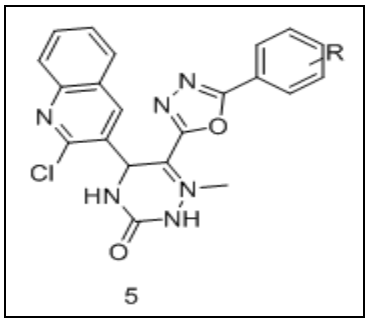
Antimicrobial Activity: Researches on 1, 3, 4-oxadiazole and their derivatives have shown that they have very prominent anti-microbial activity against a wide range of microbes.

Godhani *et al.,* (2019) synthesized a series of dihydropyrimidine substituted 1, 3, 4-oxadiazole derivatives by cyclization of carbohydrazide using phosphoryl chloride and benzoic acid in acidic condition. Every compound was primary assessed for their *in-vitro* antimicrobial activities against five bacterial strains *viz*. [*Staphylococcus aureus* (MRSA; ATCC 43300), *Klebsiella pneumoniae* (ATCC 700603), Escherichia coli (ATCC 25922), *Acinetobacter baumannii* (ATCC 19606), *Pseudomonas aeruginosa* (ATCC 27853)] and two fungi Strains *viz*. [*Candida albicans* (ATCC 90028), *Cryptococcus neoformans* var. grubii (H99; ATCC 208821)] [5].



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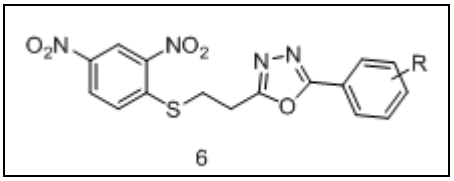
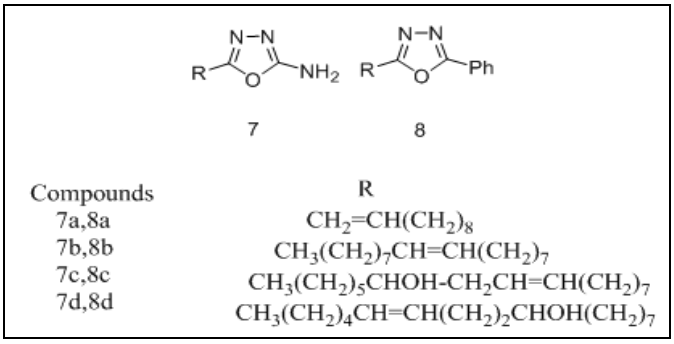
Triloknadh *et al.,* **(**2018) Synthesis of novel series of 2,4-dinitrophenyl ring containing 1,3,4-oxa-diazole and 1,2,4-triazolo[3,4-b]1,3,4-thiadiazole and their antimicrobial studies. Their antimicrobial studies have been done against four bacterial strains and the derivatives were very potent [6].



6

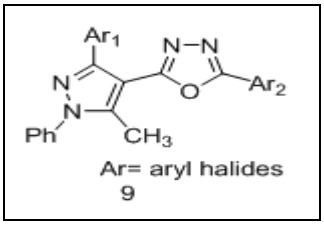
Mudasir R. Banday *et al.,* (2010) synthesized 5-(alkenyl)- 2amino-1,3,4-oxadiazoles 6a-d and 2-(alkenyl)-5-phenyl-1,3,4oxadiazole 7a-d, newly synthesized compounds were investigated for their anti-bacterial and anti-fungal activities against Gram-negative bacteria *Escherchia coli* and *Salmonella typhimurium* and Gram-positive bacteria *Staphylococcus aureus* and *Bacillus subtilis*. The investigation of the antimicrobial activity of compounds 7a–d and 8a–d revealed that all the synthesized compounds showed moderate to good antibacterial activity against *E. coli*. Compound 7d was active against all the bacteria whereas 8c was active against *E. coli*, *S. typhimurium* and *B. subtilis*. Compounds 8a, 8c and 8d also showed promising results against *E. coli* [7].



7 8

Compounds	R
7a,8a	$CH_2=CH(CH_2)_8$
7b,8b	$CH_3(CH_2)_7CH=CH(CH_2)_7$
7c,8c	$CH_3(CH_2)_5CHOH\text{-}CH_2CH=CH(CH_2)_7$
7d,8d	$CH_3(CH_2)_4CH=CH(CH_2)_2CHOH(CH_2)_7$

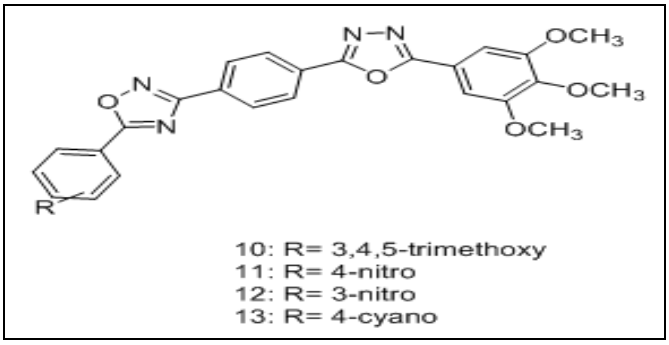
Ningaiah S, *et al*., (2014) were synthesised a novel series of 2-(5-methyl-1, 3-diphenyl-1H-pyrazol-4-yl)-5- phenyl-1,3,4-oxadiazoles and evaluated for antimicrobial activity [8].



Ar= aryl halides

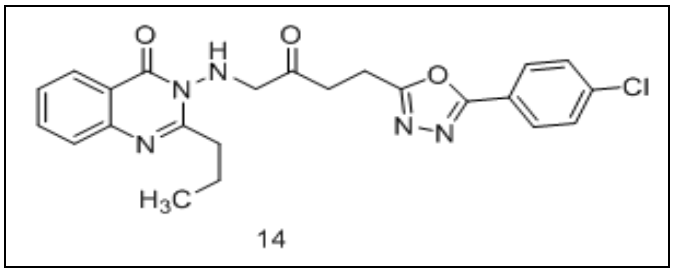
9

Anti-cancer Activity: Polothi and his research team members in the year (2019) designed and synthesized new hybrids containing the 1, 3, 4-oxadiazole with 1,2,4- oxadiazolering systems. The synthesized compounds were confirmed by ^{1}H NMR, ^{13}CNMR and mass spectroscopic techniques [9].



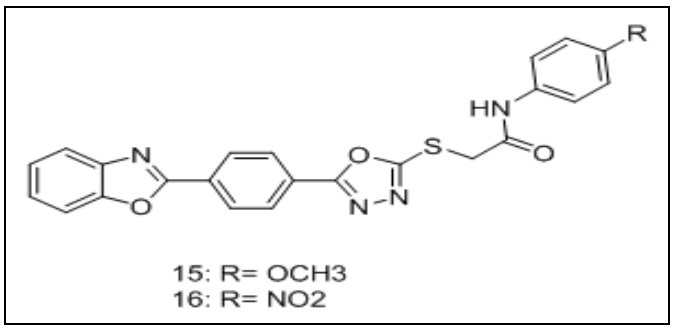
10: R= 3,4,5-trimethoxy
11: R= 4-nitro
12: R= 3-nitro
13: R= 4-cyano

Farshid and co-workers (2019) reported a multi-step reaction procedure for the synthesis of some quinazolinone-1,3,4-oxadiazole derivatives. Numbers of quinazolinone-5-(4- chlorophenyl)-1, 3, 4-oxadiazole conjugates were synthesized by the reaction of the 3-amino-4(3H) quinazolinone derivatives with 5-(4-chlorophenyl)-1, 3, 4-oxadiazole-2-thiol followed with some intermediary steps in dry acetone and potassium carbonates. Compound 2-(5-(4-chlorophenyl)- 1, 3, 4-oxadiazol-2-ylthio) N-(4-oxo-2-propylquinazolin)3(4H) acatamide showed the highest cytotoxicity with IC_{50} value of 7.52 µM against the HeLa cell line [10].



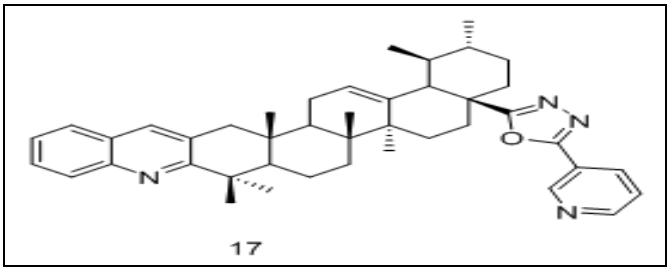
14

Ravinaik *et al.*, (2019) synthesized a novel series of amide 1, 3, 4–oxadiazole-linked benzoxazole derivatives and their structures were supported by spectral data. Synthesized compounds were screened against four human cancer cell lines, including A549, MCF7, A375, and HT-29 using Combretastatin-A4 as a control drug. Compounds N1-(4-Methoxyphenyl)-2-{5-[4-(1,3-benzoxazol-2-yl)phenyl]-1,3,4-oxadiazol-2-ylsulfanyl}acetamide and N1-(4-Nitrophenyl)-2-{5- [4- (1, 3-benzoxazol-2- yl)- phenyl]- 1, 3, 4-oxadiazol- 2- ylsulfanyl} acetamide showed higher anticancer activity than the standard drug, against HT29 cancer cell line with IC_{50} values of 0.018 and 0.093 µM [11].



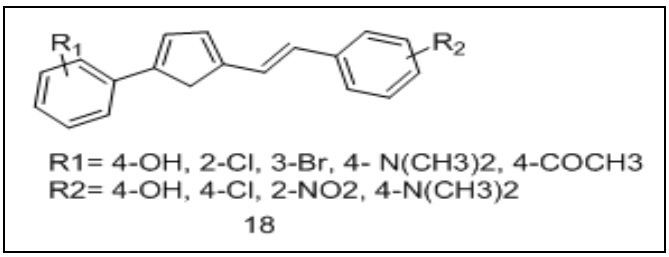
15: R= OCH3
16: R= NO2

Gu W *et al.*, (2017) designed and synthesized new series quinoline derivatives of ursolic acid and were tested for *in-vitro* anti-cancer activity against MDA-MB-231, HeLa and SMMC-7721 cell lines [12].



17

Roy PP, *et al.*, (2017) were synthesized some novel 2, 5- disubstituted 1, 3, 4-Oxadiazole derivatives using different aromatic benzaldehyde and evaluated for their anticancer activity against Ehrlich Ascites Carcinoma (EAC) bearing albino mice [13].



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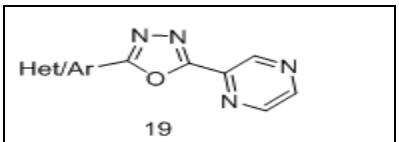
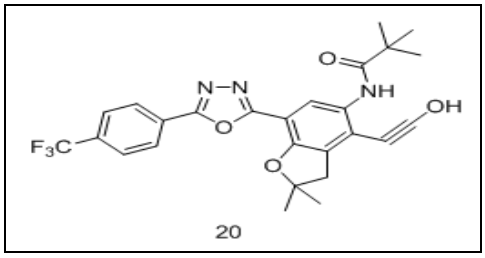
Antitubercular Activity: Armakovic and co-workers **(**2018) reported molecules containing 1, 3, 4-oxadiazole moiety attached to a pyrazine ring. The molecule with unsubstituted phenyl ring (19a) and the one with furan ring (19b) displayed activity of 1.6 µg/ml, while the most active molecules of the series, 19c, 19d and 19e displayed inhibitory activity of 0.8 µg/ml, which was 4 times more active than the reference, pyrazinamide [14-16].



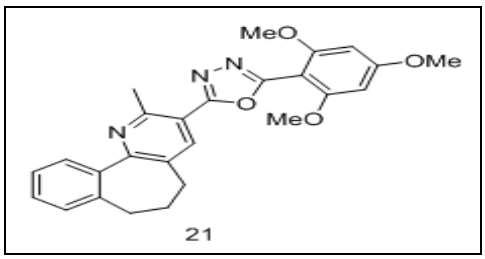
19
19a: Ar: Phenyl
19b: Het: 2-Furo
19c: Ar: 2-Cl Phenyl
19d: Ar: 3-Cl Phenyl
19e: Ar: 3-NO2 Phenyl

Gholap *et al.*, (2018) combined 1, 3, 4-oxadiazole with trifluoromethylphenyl and benzofuranylamide moieties and tested these compounds for their antimycobacterial potential. These compounds exhibited MIC values in the range of 2-24 µg/ml with the most active compound, displaying an IC_{90} of 5.7 µM against dormant Mtb H37Ra. The compounds were observed to be non-toxic to host cells when tested against the cell lines THP-1, A549 and PANC-1 [17].



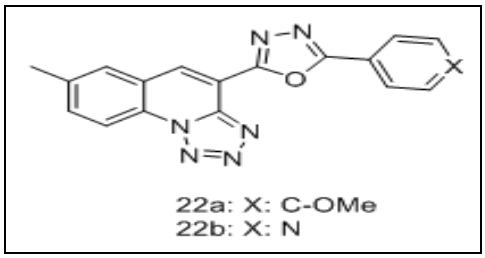
20

Sajja *et al.,* (2017) developed a series of molecules which were composed by fusion of a pyridine-oxadiazole moiety with a benzocycloheptane ring system. This design was conceived by replacing the pyridine ring of isoniazid with benzo 6, 7 cyclohepta [1,2-b]pyridine and replacing the hydrazide fragment with oxadiazole. Molecule 21 displayed the highest inhibitory activity of 1.56 µg/ml. The presence of methoxy group/s on phenyl ring attached to the oxadiazole moiety was found to be crucial for antituberculosis activity [18].



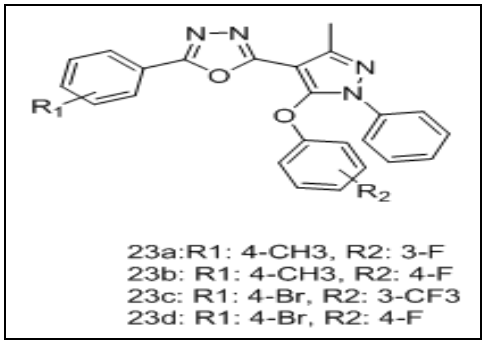
21

Sapariya *et al.,* (2017) Synthesized of 7-substituted tetrazolo [1,5-a] quinolines incorporating 1,3,4-oxadiazole nucleus. The *in-vitro* antituberculosis activity was carried out at 100 µg/ml concentration, molecules 22a and 22b displayed more than 90% inhibition at this concentration [19].



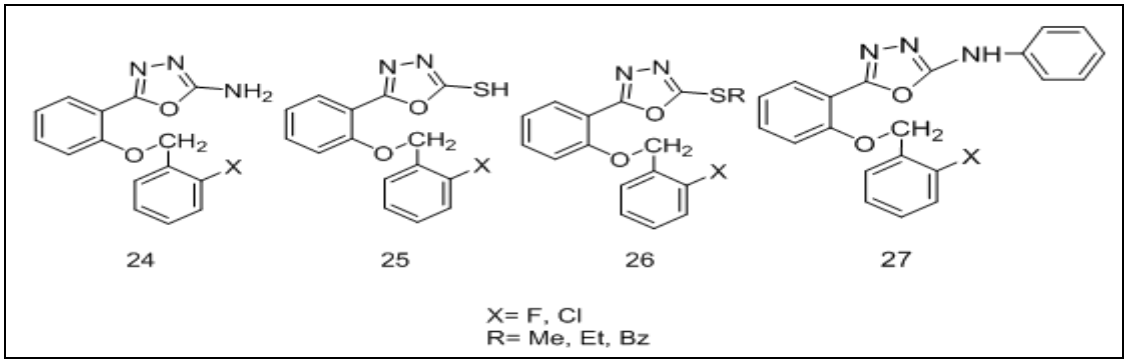
22a: X: C-OMe
22b: X: N

Karad *et al.,* (2016) explored the biological applications of fluoro substituted pyrazole nucleus clubbed with 1, 3, 4-oxadiazole scaffolds, antituberculosis activity being one of the important potential applications. The molecules were designed by making the hybridization of pyrazole and 1,3,4-oxadiazole moieties. Antituberculosis screening of all the synthesized molecules was conducted, and four molecules, 23a-23d, were found to display more than 90% inhibition at 250 µg/ml [20].



23a:R1: 4-CH3, R2: 3-F
23b: R1: 4-CH3, R2: 4-F
23c: R1: 4-Br, R2: 3-CF3
23d: R1: 4-Br, R2: 4-F

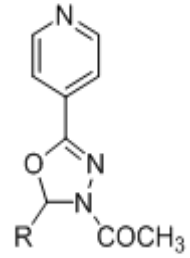
Anti-convulsant Activity: Afshin Zarghi *et al.,* (2008) synthesized 2- amino- 5- (2- halo- 2 benzyl-oxyphenyl)- 1,3,4-oxadiazoles 13, 5-(2-Halo-2 benzyloxyphenyl)-2-mercapto-1,3,4-oxadiazole 14, 2Alkylthio-5-(2-halo-2-benzyloxyphenyl)- 1, 3, 4-oxadiazole [26] and 2-Anilino-5-(2-halo-2-benzyl-oxyphenyl)- 1,3,4-oxadiazole [27], newly synthesized compounds were investigated for anticonvulsant evaluations by qualitative assays using MES (maximal electroshock) and PTZ (pentylene-tetrazole) tests. The first assay is related to the induction of seizure electrically and the second induction of seizure is made chemically using adult male albino mice (25-30g). The compound 27, which has amino group on 2 positions of oxadiazole ring and fluoro substituent at the ortho position of benzyloxy group, has shown the best anticonvulsant activity in PTZ and MES models [21].



24 25 26 27

X= F, Cl
R= Me, Et, Bz

Sadaf Jamal Gilani *et al.*, (2009) synthesized 1-(2-(2substitutedphenyl)-5-(pyridine-4-yl)-1, 3, 4- oxa-diazol-3(2H)yl)ethanone 17a-h, newly synthesized compounds were investigated for anti-convulsant evaluations by qualitative assays using MES (maximal electroshock) and scPTZ (subcutaneous pentylenetetrazole) tests using adult male albino mice (25-30 g). A 30mg/kg dose was given to mice during MES test, which showed protection in half-tested mice were 28a, 28c, 28f & 28g after 0.5h interval of time. These compounds have shown protection after 4h but at a higher dose of 100mg/kg. The compounds 28b, 28d & 28e have shown protection at a dose of 100mg/kg after duration of 0.5 h. These compounds have also shown protection effect but after a duration of 4 hours and also at a higher dose of 300mg/kg. The compound 20h has shown protection in the MES test at a dose of 300mg/kg at 0.5 hr as well as 4 h. In the scPTZ the compounds 28a, 28c & 28g have shown the activity at a dose level of 30mg/kg dose level after an interval of 0.5h and 100mg/kg levels after an interval of 4hr, but compound 28f has shown the same activity at a dose 100mg/kg at 0.5 h time interval. These compounds have also shown protection at a higher dose of 300mg/kg after 4 h interval. The rest compounds 28b, 28e & 28h have shown the activity at both time intervals but at a dose of 300mg/kg [22].

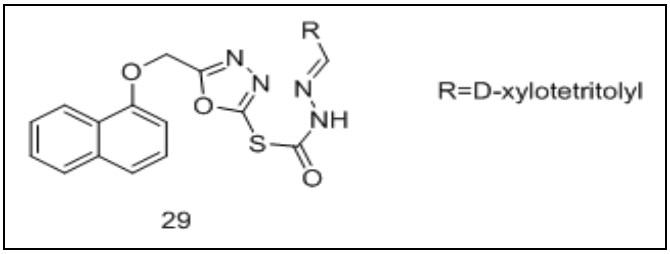


28

R

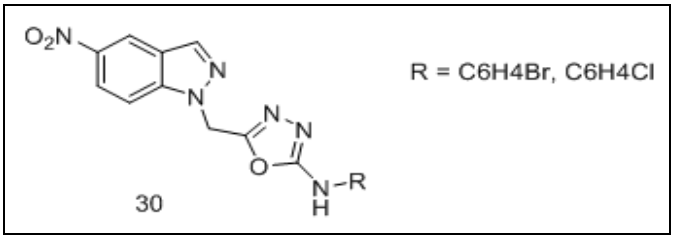
a= o-C_6H_5Cl
b= p-C_6H_5Cl
c= o-C_6H_5OH
d= m-C_6H_5OH
e= p-$C_6H_5OCH_3$
f= p-C_6H_5F
g= o-$C_6H_5NO_2$
h= p-$C_6H_5N(CH_3)_2$

Anti-HIV Activity: El-Sayed WA, (2009) The newly synthesized compounds were evaluated for their HIV inhibitory activity as reverse trans-criptase inhibitors by using microtiter anti-HIV assays with CEM-SS cells or fresh human peri-pheral blood mononuclear cells. Compound 29 showed the highest activity with an IC_{50} value of 1.44 μM [23].



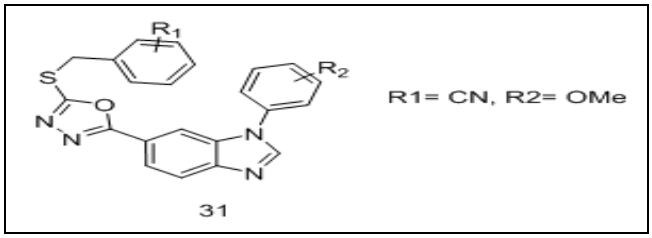
29

Antipyretic Activity: Cheptea C, (2012) Synthesized a series of 2 - (5'- nitroindazole - 1'-methyl)] – 5 - (pbromophenylamino)-1, 3, 4-oxadiazole derivatives. All synthesized compound showed remarkable antipyretic activity, similar to that of acetylsalicylic acid [24].



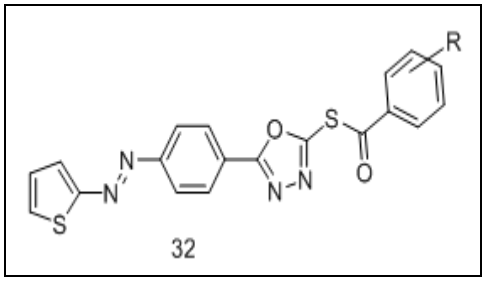
30

Anti-Alzheimer's Activity: Saitoh M, (2009) Synthesized series and derivatives of 3-[({5-[1-(4-Methoxyphenyl) - 1H – benzimidazol – 6 - yl 1, 3, 4-oxadiazolyl} sulfanyl) methyl benzonitrile. Among these compound 20x showed highly selective and potent GSK-3β inhibitory activity *in-vitro* [25].



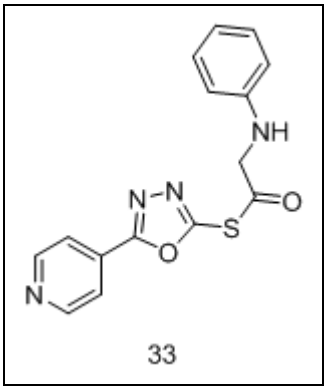
31

Anti Fungal and Anti Bacterial Activity: Desai NC, *et al.*, YM (2014) were synthesised novel series of 2-{5-[4-(1-aza-2-(2-thienyl) vinyl) phenyl] (1,3,4- oxa-diazol-2-ylthio)}-N-arylacetamides and screened for their antibacterial and antifungal activities [26].



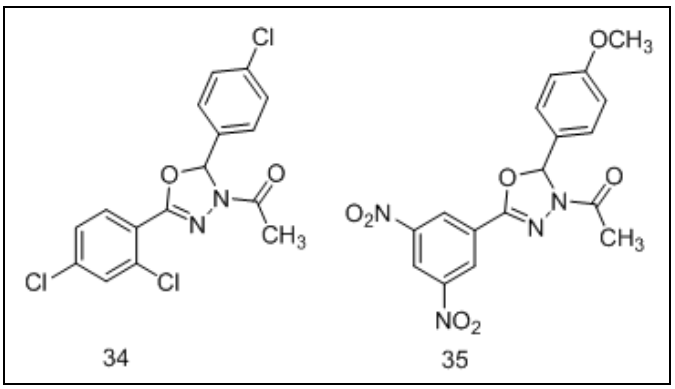
32

Raval JP, *et al.,* (2011) were synthesized a series of 2 (4-pyridyl)- 5[(aryl/heteroarylamino)-1-oxoethyl] thio-1, 3, 4- oxadiazole and evaluated for antibacterial activity [27].



33

Lole *et al.,* (2016) synthesized novel 1, 3, 4-oxadiazole derivatives and evaluated their antibacterial activity against *E. coli* and *S. aureus*. Streptomycin, as in previous research, was used as reference compound. The compounds 34 and 35 showed moderate activity against *E. coli* (ZOI = 12 mm, streptomycin ZOI = 15 mm). Compound 35 displayed good activity against *S. aureus* (ZOI = 12 mm), while streptomycin showed zone of inhibition growth (ZOI = 13 mm). The activity of these compounds was enhanced due to the substitution of electron-withdrawing groups NO2 and chlorine atom at para position in the phenyl ring [28].



34 35

CONCLUSION: The review has concluded with the important therapeutic activities of the 1,3,4-oxadiazole. This review paper comprises all the major biological activity of 1,3,4-oxadiazole, and it can be used for further researches. The major activities of 1,3,4-oxadiazole are anti-microbial, anti-inflammatory, analgesic, anti-tumour, anti-convulsant, anti-HIV, anticancer, anti Alzheimer's, antioxidant and antipyretic activities.

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