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An Illustrated Review on Chemical Properties, Synthetic Methods and Biological Activities of Quinazolines

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ABSTRACT

Biologically active heterocyclic compounds comprise of largest & manifold family of organic compounds. These compounds include Quinolines, Quinazolines, Aminoquinolines, etc and their derivatives. They exhibit multifaceted biological properties like analgesic, anti-inflammatory, anticonvulsant, antibacterial, antifungal, antidepressant, anticancer, antitubercular &antihistaminic. Biologically active heterocyclic compounds are considered to be important as they are highly utilized pharmacological molecules. These compounds have various physiological significance too. This review summarizes chemical characteristics, possible synthetic routes & various bioactivities of quinazolines.

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INTRODUCTION

Organic compounds which contain rings unfurled of carbon & heteroatoms such as nitrogen, sulfur & oxygen are entailed heterocyclic compounds. spectacular synthesis, properties, and applications of heterocycles mainly used for drug designing come under heterocyclic chemistry. In medicinal chemistry commonly synthesized biologically active heterocyclic moiety includes quinine, quinolines, aminoquinolines & quinazolines, etc. They are useful in treating various disease conditions. They are widely used for medicinal purposes in the pharmacological industry with marginal side effects. They are also manufactured & assessed for their biological pursuit. Quinolines and quinazolines-containing drugs are widely used in pharmacological industries. In near future, they would probably replace many other organic-based pharmaceuticals [1].

Quinazolines are major nitrogen-based aromatic heterocyclic compounds. Benzene & pyrimidine ring fused to form quinazoline. Quinazolines possess a broad range of biological activities. Over the past 200 years, they have to allure remarkable attention from researchers. Till now approximately 150 naturally occurring quinazoline derivatives are introduced which have been derived from different plants, animals, microorganisms & many of them from anthranilic acid [2]. Vaccine (Paganini) was the first quinazoline which was isolated in 1888, from *Adhatodavasica.* Later, it was isolated from other species too. Derivatives of quinazoline hold broad-spectrum biological properties such as anti-cancer, anti-inflammation, anti-bacterial, analgesic, antivirus, anti cytotoxic, antispam, antitubercular, antioxidation, anti-plasmodial, antihypertensive, antiobesity, antipsychotic, antidiabetics, etc. Along with the vast number of biological properties, various synthetic routes are also there for the synthesis of quinazolines and their deriva-

tives. This review covers various synthetic methods, chemical reactions & various bio-activities of quinazolines [3].

Chemical Properties of Quinazolines

In 1957, Williamson appraises quinazoline's chemistry which was further reviewed in 1958 & 1963 by Lindquist &Armarego. In acid (cold, dilute) & alkaline solution quinazoline is stable whereas when these acid & alkali solutions are heated, it gets destroyed. Formation of 2- Formylaniline, NH_3 & Methanoic acid takes place when quinazolines are boiled which Muriatic acid (HCl). Quinazoline undergoes oxidation with $KMnO_4$ & results in the formation of Pyrimidine-4,5-dicarboxylic acid. The reaction of quinazoline in dil. Aq. Acid with H_2O gives 3,4-Dihydro-4-oxoquinazoline. Quinazoline undergoes reduction with HgNa to form 1,2,3,4-tetrahydro quinazoline whereas with $LiAlH_4$ it forms 3,4-Dihydroquinazoline. Electronic substitution in Quinazolinesoccurs only by nitration in the presence of con.H_2SO_4 & con. HNO_3 results in the formation of 6-Nitroquinazoline. Quinazoline undergoes nucleophilic substitution with NH_2NH_2 (Hydrazine) and $NaNH_2$ (Sodamide) which results in the formation of 4-Quinazolinamine & Hydralazine. Alkylation alters the drug's biological properties [4]. Alkylation usually takes place as to the nitrogen atom, 3-methyl, 3-ethyl, 3-alkyl & 3-benzylquinazolinium salts & results in information of 4-alkoxy-3-alkyl-3,4dihydro quinazolinium salts. Figure 1 depicts a diagrammatic representation of the chemistry of Quinazolines.

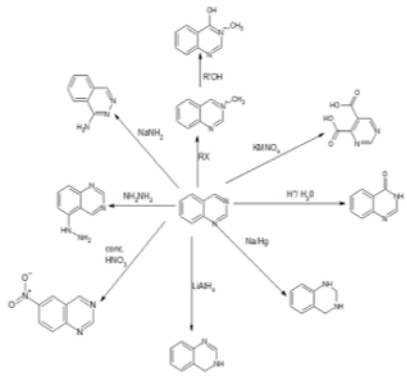


Figure 1: Chemical reactions of quinazoline

Methods for Synthesis of Quinazoline & its Derivatives

Synthesis of 2-phenyl quinazoline: Amino benzophenone & benzylamine are catalyzed [Figure 2] by ceric ammonium nitrate (CAN)-TBPH in CH_3CN to give 2- phenyl quinazoline [4].

Synthesis of 2-aryl quinazoline: 2-bromophenyl methyl amines &aryl amides catalyzed in the presence of ligand-free copper to synthesize 2-aryl quinazoline [Figure 3] [5].

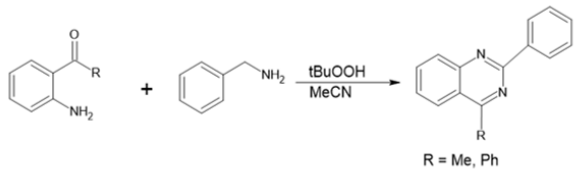


Figure 2: Scheme 1 Synthesis of 2-phenyl quinazoline

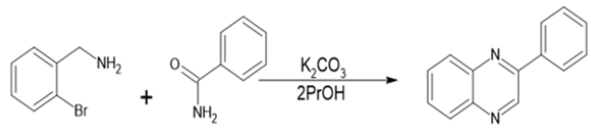


Figure 3: Scheme 2 Synthesis of 2-aryl quinazoline

Synthesis of 3,4-dihydro-4-oxoquinazoline: 3 or 4-substituted 2-Aminobenzenecarboxylic acid at 125-130ºC react with methanamide to synthesize 3,4-dihydro-4-oxoquinazoline. It is also known as *Niementowski's synthesis* (Figure 4) [6].

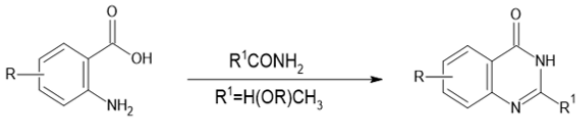


Figure 4: Scheme 3 Synthesis of 3, 4-dihydro-4-oxoquinazoline

Synthesis of 2-propyl and 2-isopropyl-3,4-dihydro-4-oxo-quinazoline: Normal or isobutyrylanilides solution is boiled with ethyl carbamate &Diphosphorus pentoxide in dimethyl benzene (xylene) to give 2-propyl and 2-isopropyl-3,4-dihydro-4oxoquinazolines. It is also known as *Sen & Ray's Synthesis* (Figure 5) [7].

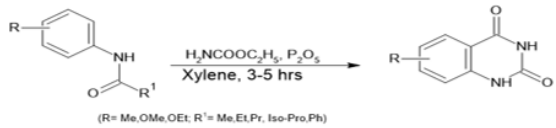


Figure 5: Scheme 4 Synthesis of 2-propyl and 2-isopropyl-3, 4-dihydro-4-oxo-quinazoline

Synthesis of 2-aryl-4-amino quinazolines: Isonitriles and N-aryl amidines undergo reaction in the presence of Pd-catalyzed intramolecular aryl C(sp^2)–H amidination by the introduction of methyl cyanide (Figure 6) [8].

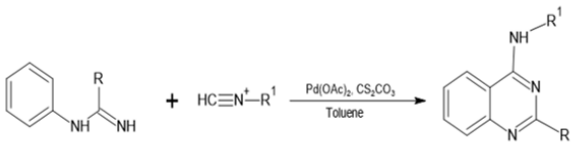


Figure 6: Scheme 5 Synthesis of 2-aryl-4-amino quinazolines

Synthesis of functionalized Quinazoline having no radicals: It takes place by microwave-promoted chemical reaction of benzaldehyde-O-phenyl-oxime & aldehyde in the presence of zinc chloride (Figure 7) [9].

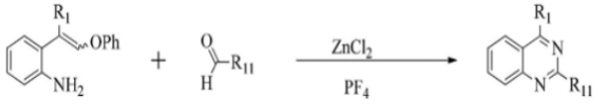


Figure 7: Scheme 6 Synthesis of functionalized Quinazoline having no radicals

Synthesis of 2, 4-disubstituted Quinazoline: It is done by microwave-promoted cyclization. Acyl amides undergo reaction in the presence of formic acid ammonium salt to synthesize 2, 4-disubstituted Quinazoline (Figure 8) [10].

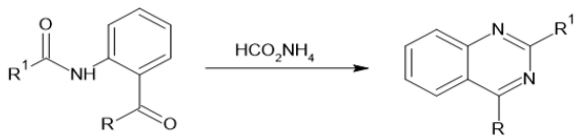


Figure 8: Scheme 7 Synthesis of 2, 4-disubstituted Quinazoline

Synthesis of Benzoyleneurea: Anthranilic acid reacts with urea which results in the formation of Benzoyleneurea (Figure 9) 2-Aminobenzoic acid & KOCN are used to prepare O-Ureidobenzoic acid which is then cyclized by heating with acid or alkali to form Benzoyleneurea (Figure 10). α-Isatin oxime when heated with dil. NaOH rearranges itself to form Benzoyleneurea (Figure 11) [11].

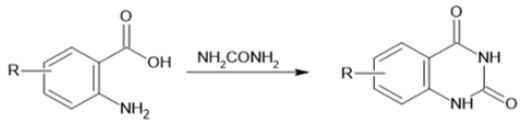


Figure 9: Scheme 8-a Synthesis of 2, 4(1H, 3H)-Quinazoline Dione

Synthesis of 3-(2-chlorobenzylidene)- 1,2,3,9-tetrahydropyrrolo - 2 quinazoline: α - Amino - o - toluidine react with gamma-Butyrolactone & form an intermediate compound which then condensed with Benzoic aldehyde to form "3-(2-chlorobenzylidene)-1,2,3,9-tetrahydropyrrolo-2quinazoline" (Figure 12) [12].

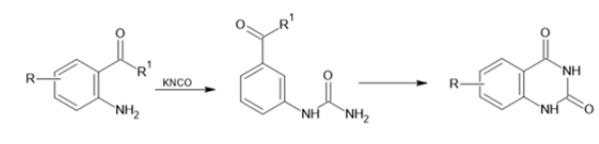


Figure 10: Scheme 8-b Synthesis of 2, 4(1H, 3H)-Quinazoline Dione

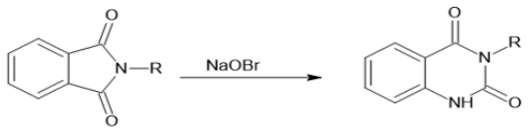


Figure 11: Scheme 8-c Synthesis of 2, 4(1H,3H)-Quinazoline Dione

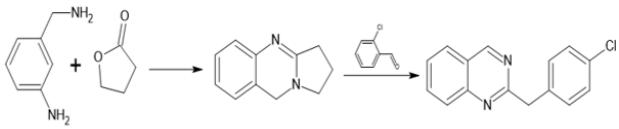


Figure 12: Scheme 9 Synthesis of 3-(2-chlorobenzylidene)-1,2,3,9-tetrahydropyrrolo-2quinazoline

Synthesis of 7-chloro-3-phenyl- [1, 2, 3] triazolo[1,5-a] quinazoline-5-one: Benzoic acid,2-azido-4-chloro react with benzyl cyanide to form"7-chloro-3-phenyl- [1, 2, 3] triazolo[1,5-a] quinazoline-5-one" (Figure 13) [10].

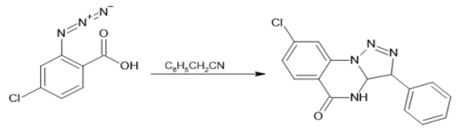


Figure 13: Scheme 10 Synthesis of 7-chloro-3-phenyl- [1, 2,3] triazolo[1,5-a] quinazoline-5-one

Synthesis of 2,4-dichloroquinazoline: Benzoyleneurea undergoes reaction in the presence of phosphoryl chloride & DIPEA (Diisopropylethylamine) to synthesize 2,4-dichloroquinazoline (Figure 14) [13].

Biological Activities of Quinazolines

Quinazoline compounds are frequently used com-

Figure 14: Scheme 11 Synthesis of 2,4-dichloroquinazoline

pounds for their bioactivities. They are the requirement of the chemist & medicinal industry [14]. In this part, various bioactivities of quinazoline compounds are highlighted (Figure 15).

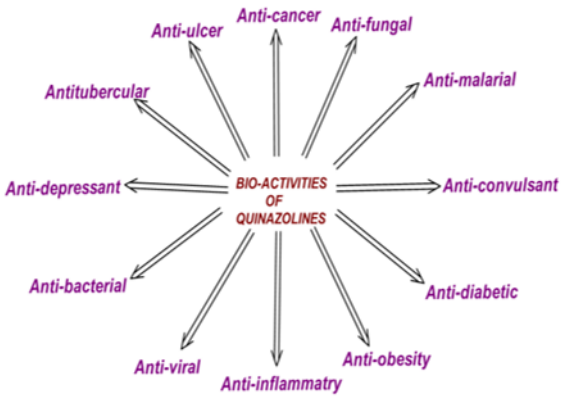


Figure 15: Bio-activities of quinazoline

Anticancer activity

Cancer is a major health problem that causes abnormal growth of cells in the body. These cells are known as malignant or tumor cells.'2-aryl quinazolinones' containing (E)- stilbene moiety which exhibits anticancerous activity as opposed to carcinoma cell lines of humans. Primary amine substituted quinazoline linked benzimidazole which show anticancer usage as opposed to colon plus prostate cancer cell lines. Conjugates of phenyl N-mustard-quinazoline were synthesized & reported for their anti-cancer activity. Conjugates of 6-substituted quinazolinone containing 4-(2-fluorophenyl) piperazine-1-yl moiety were synthesized & its anti-cancerous activity is assessed by using: HT29, HCT116 & normal human lymphocytes. 3-(4-chlorophenyl)-2-phenylquinazoline-4(3H)-one (12a), 3-(3-chlorophenyl)-2-phenylquinazoline-4(3H)-one (12b) & 2-phenyl-3-p-tolyquinazoline-4(3H)-one (12c) which show anticancerous activity opposed to MCF-7 carcinoma cell line (Figure 16) [15].

Antidiabetic activity

Quinazoline-1-deoxynijirimycin hybrids act as the most efficacious inhibitor of α-glucosidase (Figure 17) [16].

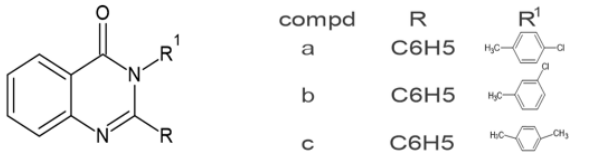


Figure 16: Scheme 12 Anti-cancerous activity of Quinazolines

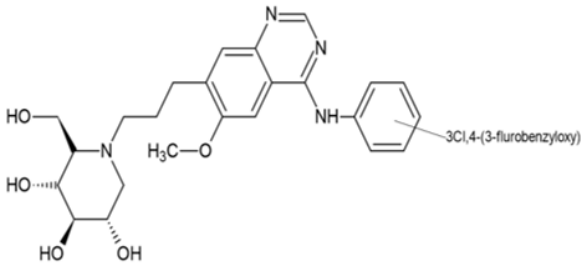


Figure 17: Antidiabetic activity of Quinazolines

Antimalarial activity

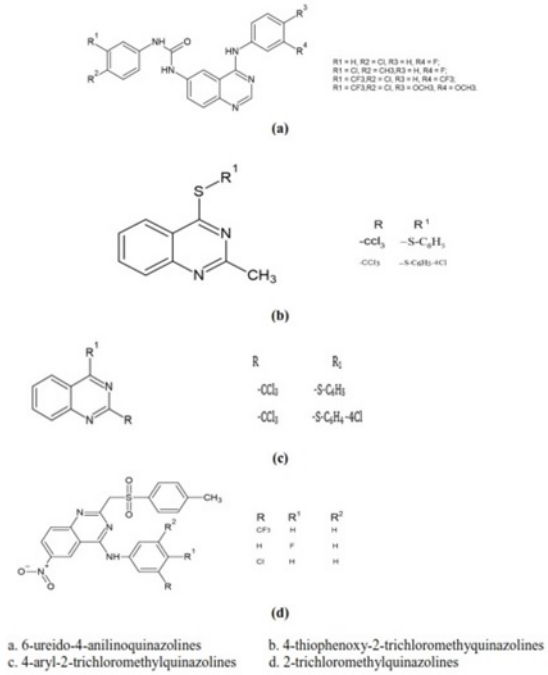
Series of 6-ureido-4-anilinoquinazolines (13a) which possess antimalarial activity. Synthesis of derivatives of 4-thiophenoxy-2-trichloromethyquinazolines (13b) which exhibits antimalarial activity against *P. falciparum*. Synthesis of derivatives of 4-aryl-2-trichloromethylquinazolines was also reported to exhibit antiplasmodial activity. The synthesized series of derivatives of quinazoline exhibit antimalarial property. Synthesis of 4-thiophenoxy-2-trichloromethyquinazolines (13c) which was found to be the most potent antimalarial agent. Chloroquine phosphate &doxycline were taken as testimonial drugs. Antimalarial activity of 2-trichloromethylquinazolines (13d) newly substituted quinazoline having phenoxy group at 3^{rd} position was synthesized by them. It exhibits potent activity towards *P. Falciparum* (Figure 18) [17].

Antidepressant & Anticonvulsant activity

Derivatives of 3-[5-substituted1,3,4-thiadiazole2-yl]-2-styrylquinazoline-4(3H)-one (19a) was reported for their CNS depressant and anticonvulsant activity.

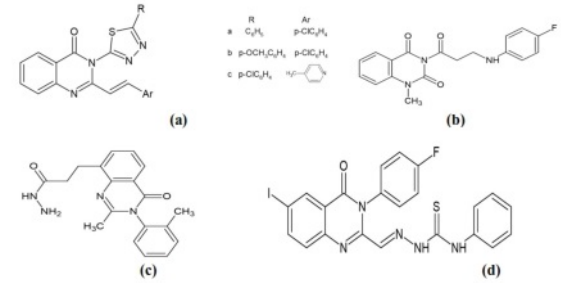
Derivatives of N-substituted methyl Benzoyleneurea (19b) were synthesized were reported as the most potent anticonvulsant agent.

Series of "7-substituted-4(3H)-quinazolinone (19c) which exhibit anticonvulsant activity. Synthesis of 4(3H)-quinazolinone-2-carboxaldehyde (19d) which exhibits anticonvulsant activity (Figure 19) [18].



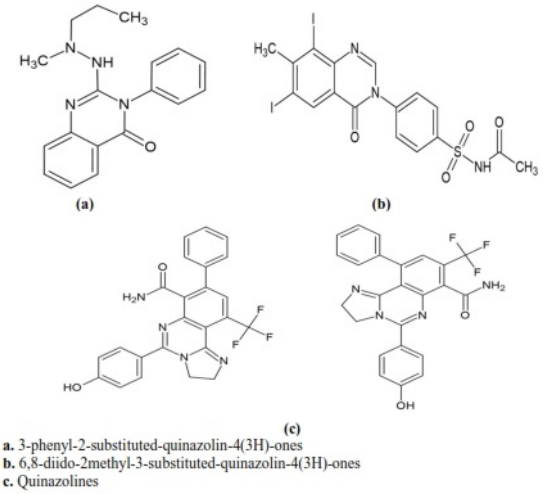
a. 6-ureido-4-anilinoquinazolines
b. 4-thiophenoxy-2-trichloromethyquinazolines
c. 4-aryl-2-trichloromethylquinazolines
d. 2-trichloromethylquinazolines

Figure 18: Scheme 13 Antimalarial activity of Quinazolines



a. 3-[5-substituted1,3,4-thiadiazole2-yl]-2-styrylquinazoline-4(3H)
b. Methyl Benzoylene urea
c. 7-substituted-4(3H)-quinazolinone
d. Synthesis of 4(3H)-quinazolinone-2-carboxaldehyde

Figure 19: Scheme 14 Antidepressant & Anticonvulsant activity of Quinazolines



a. 3-phenyl-2-substituted-quinazolin-4(3H)-ones
b. 6,8-diido-2methyl-3-substituted-quinazolin-4(3H)-ones
c. Quinazolines

Figure 20: Scheme 15 Anti-inflammatory & Analgesic activity of Quinazolines

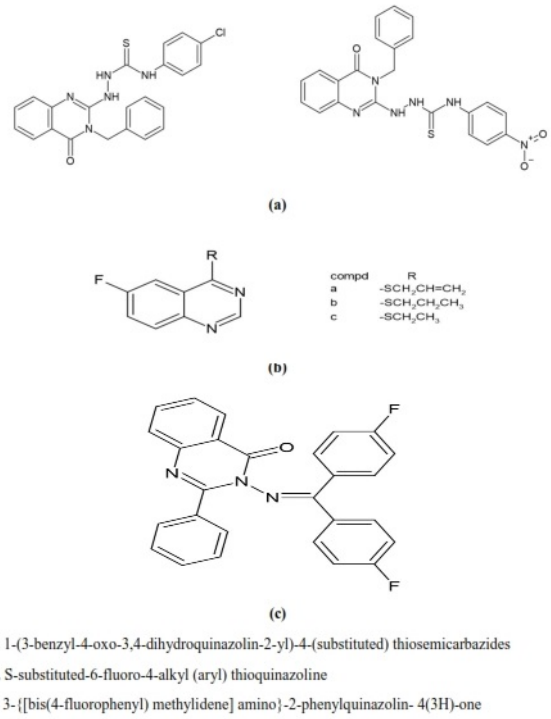


Figure 21: Scheme 16 Antifungal & Antibacterial activity of Quinazolines

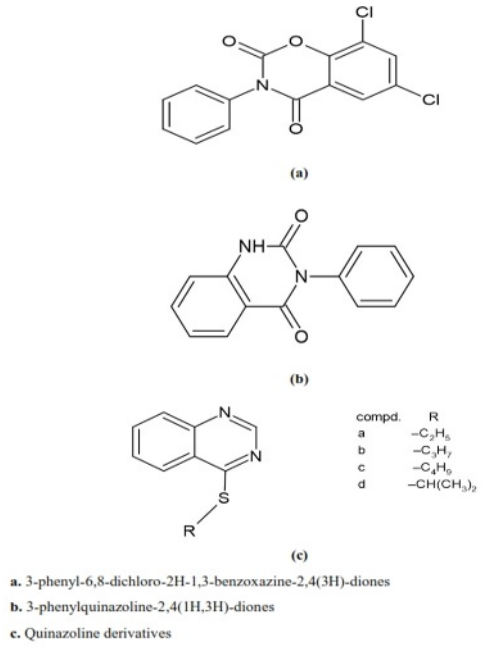
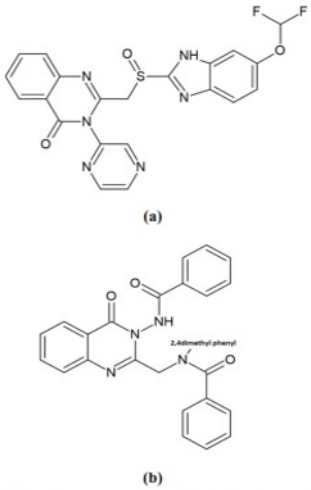


Figure 22: Scheme 17 Anti-tubercular activity of Quinazolines



a. 2-[5-substituted-10H-benzo (*d*)imidazol-2-yl sulfinyl] methyl-3-substituted quinazoline-4(3H)-ones
b. N-((3-benzamide-4-oxo-3,4-dihydroquinolin-2-yl) methyl)-N-phenyl benzamide

Figure 23: Scheme 18 Anti-ulcer activity of Quinazolines

Anti-inflammatory & Analgesic activity

The novel "3-phenyl-2-substituted-quinazolines-4(3H)-ones" (20a) for its analgesic & anti-inflammatory activity. Sulphonamides bearing derivative of "6,8-dildo-2methyl-3-substituted-quinazoline-4(3H)-ones (20b) which exhibits anti-inflammatory activity. Derivatives of novel 8/10-trifluoromethyl-substitutedimidazo quinazolines. which exhibits anti-inflammatory activity against indomethacin. Derivatives of 2,4,6-trisubstituted quinazoline (20c) and & possess the most potent anti-inflammatory activity (Figure 20) [19].

Antifungal and Anti-bacterial activity

Synthesis of derivatives of 1-(3-benzyl-4-oxo-3,4-dihydro quinazoline-2-yl)-4-(substituted) thiosemicarbazides (21a). which possess antimicrobic activity against gram +ve and gram-bacteria. The synthesized derivatives of S-substituted-6-fluoro-4-alkyl (aryl) thioquinazoline (21b) exhibit antifungal activity. "3-{[bis(4-fluorophenyl) methylidene] amino}-2-phenylquinazolin- 4(3H)-one" (21c) which exhibits antimicrobial activity against microorganisms (Figure 21) [20].

Antitubercular Activity

Synthesis of "3-phenyl-6, 8-dichloro-2H-1,3-benzoxazine-2,4(3H)-diones" (22a) & 3-phenylquinazoline-2,4(1H,3H)-diones" (22b) were reported. They were considered to be the most potent antineoplastic agents for the treatment of tuberculosis (Figure 22) [21].

Anti-ulcer Activity

Synthesis of "2-[5-substituted-1OH-benzo(*d*)imidazole-2-yl sulfinyl] methyl-3-substituted quinazoline-4(3H)-ones" (23 a) was reported for its anti-ulcer activity. Synthesis of compounds was reported & evaluated as the most potent anti-ulcer compound. To synthesize derivatives of "N-((3-benzamide-4-oxo-3,4-dihydroquinolin-2-yl) methyl)-N-phenyl benzamide" &evaluated for their antiulcer activity (Figure 23) [22].

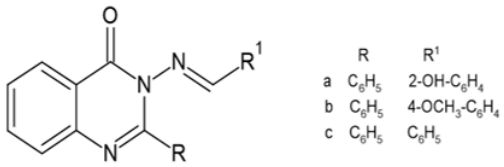


Figure 24: Scheme 19 Antiviral activity of Quinazolines

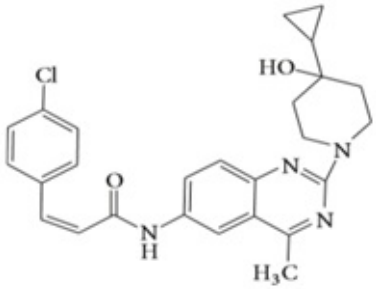


Figure 25: Scheme 20 Anti-obesity agents of Quinazolines

Antiviral Activity

Synthesis of Schiff bases of derivatives of "2-phenyl quinazoline-4(3) H-one" which exhibits antiviral property. (a) Manifest antiviral activity against HSV-1, 2 & (b), (c) against HSV-1 & vaccinia vaccine (Fig-

ure 24) [23].

Anti-obesity Agents

A series of quinazoline derivatives were synthesized & considered as a nemesis for MCHR1 (Figure 25) [24].

CONCLUSION

Many compounds exhibit anti-microbial activity so they can be used for various therapeutic exposure, biologically active heterocycles are one of them. All synthesized heterocyclic derivatives might be used for the advanced growth of other novel heterocycles. Quinazoline moiety & its derivatives are focal points of medicinal chemistry. They are highly used in medicinal sciences because of their wide range of medication activities. Several structural modifications in quinazoline moiety are done and are useful in treating various diseases. These moieties are cost-effective and highly efficient. Due to quinazolines' physiochemical possessions, they strive miscellaneous array of restorative success. Synthesis of Eco- friendly, sophisticated, nontoxic, highly efficient compounds of minimal efficacy are of great use nowadays & for the future also. Highly efficient drugs with minimum cost value are the requirement of the future, to which quinazolines are best suited.

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Conflict of interest

The authors declare that they have no conflict of interest in this study.

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