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AZETIDINE: STRUCTURAL FEATURES, SYNTHETIC APPROACHES AND THERAPEUTIC POTENTIAL

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ABSTRACT

Azetidine is a saturated four-membered nitrogen-containing heterocycle known for its ring strain, high reactivity, and versatile functionalization, making it valuable in medicinal chemistry, organic synthesis, and materials science. Extensive research has explored its synthesis, structural modification, and biological activities, revealing significant therapeutic potential, particularly antibacterial and antidiabetic effects. Various synthetic methods including cyclization, cycloaddition, metal-catalyzed reactions, multicomponent strategies, and ring-expansion routes enable efficient and stereoselective preparation of diverse azetidine derivatives. The incorporation of azetidine into pharmacophores such as β-lactams further highlights its importance due to strong antimicrobial, anticancer, anti-inflammatory, and antiviral properties.

INTRODUCTION

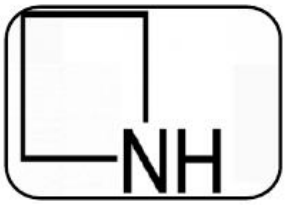


Fig.1 General structure[6]

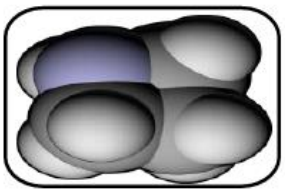


Fig.2 3d structure

Nitrogen heterocycles occupy a valuable position in pharmaceuticals owing to their broad-spectrum biological properties. More than 75% of the approved drugs bear nitrogen heterocycles, which will increase in the coming decades.[1] The synthetic value of azetidine has been further extended by developments in photo-redox catalysis, decarboxylative cross- coupling, and flow chemistry, which have made libraries of functionalized derivatives appropriate for high-throughput biological screening accessible.[2] Derivatives of azetidine have been shown to possess antibacterial and antifungal properties.[3] It has been demonstrated that pyridine derivatives possess antimicrobial properties. It was therefore anticipated that molecules containing both chemical moieties would produce substances with interesting biological characteristics. The Schiff bases were exposed to an addition reaction with chloro-acetyl chloride in the presence of 1,4dioxane and triethylamine in order to synthesize azetidine derivatives. IR and 1HNMR were performed to assess the chemical structures of the synthesized compounds. The synthesized compounds were tested for antibacterial activity against Staphylococcus aureus and Escherichia coli. The medicinal potential of azetidine is complemented by its role as a versatile intermediate in organic synthesis.[4] This comprehensive review on the polymerization of aziridine and azetidine monomers will provide a basis for the development of future macromolecular architectures using these relatively exotic monomers.[5]

Synthetic Schemes

Scheme 1

Synthesis of azetidine from imines-This reaction scheme depicts the multi-step synthesis of a Azetidine derivative from a naphthoquinone starting material and an aromatic amine, using ethanol (EtOH), dimethylformamide (DMF), and piperidine (Pip.) as solvents/catalysts, followed by cyclization with thioglycolic acid (SHCH2COOH). The process features both condensation and cyclization, commonly

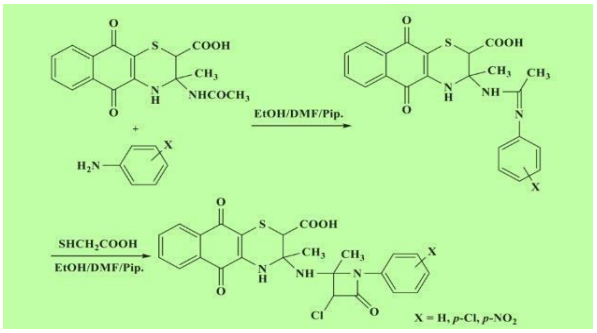


Fig. 3: Synthesis of azetidine from imines.

Used in azetidine synthesis. Piperidine acts as a base catalyst, and DMF/EtOH aid solubility and reaction rate. The final product contains a azetidine moiety fused often evaluated bioactivity.[7]

Scheme 2

synthesis of azetidines from imines and carbon monoxide. The multicomponent technique was directly adaptable to structural diversity. The beta- lactams were easily synthesized using a variety of acid chlorides and imines, all of which produced a trans-isomer in good yields. Both alkyl and aryl acid chlorides were utilized. However, beta lactam yields fell with EWGs on imines. The palladium-catalyzed carbonylation of allyl phosphate with imines under

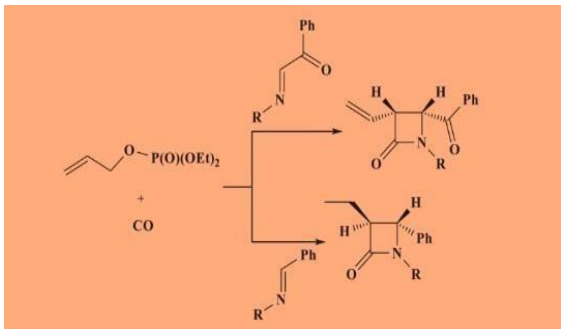


Fig. 4: Synthesis Of Azetidines From Imines And Carbon Monoxide.

Carbon monoxide pressure was a highly stereo selective reaction since it produced both cis and trans isomers. This reaction shows the [2+2] cycloaddition (carbonylation) reaction between an allyl phosphonate and carbon monoxide (CO) in the presence of an imine (Schiff base) derivative, resulting in the creation of four-membered cyclic amides known as β-lactam derivatives. When CO enters the reaction system, the imine acts as a source of nitrogen for, The reaction involves the production of rings and a metal-catalyzed carbonylation route, resulting in highly stereoselective β-lactams. Many antibiotics, such as penicillin and cephalosporins, rely on β-lactam molecules as their structural components.[8]

Scheme 3

Synthesis of azetidine by metal catalyzed cycloaddition of imines to alkene. The cycloaddition of imines (C=N) and alkenes (C=C) is a primary method for creating azetidines.Normally, simply heating imines and alkenes together won't cause them to react because of certain symmetry rules. Instead, scientists use light, or catalysts like photo redox catalysts or Lewis-acids to make the reaction happen. These catalysts usually create intermediate compounds, such as diradicals or iminium ions, along the way.

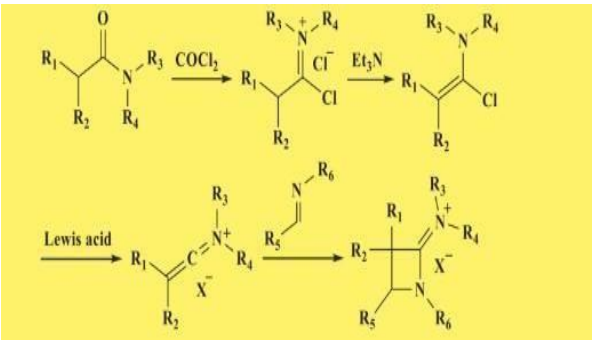


Fig. 5: synthesis of azetidine by metal catalyzed cycloaddition of imines toalkene.

The cycloaddition of ketenimines with imines was performed under the lewis catalysis, the ketenimine salts, obtained from tertiary carboxamides, were subjected to cyclo- condensation with imines to afford the 2-azetidiniminium salts with trans- stereoselectivity.[9]

Scheme 4

Synthesis of azetidine by cycloaddition of imines to carbonyl compounds (by using (NaHMDS)

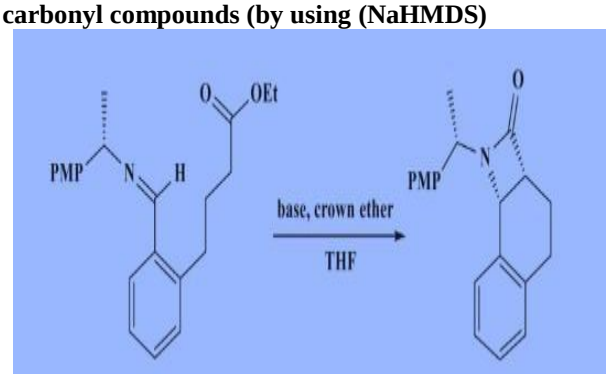


Fig. 6: Synthesis of azetidine by of imines to carbonyl compounds.

Reaction conditions have an impact on the synthesis of azetidines by the intramolecular cycloaddition of an imine to a carbonyl moiety employing a strong base, such as NaHMDS or LiHMDS.

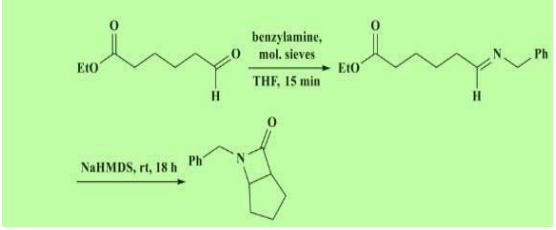


Fig. 7: Synthesis of azetidine by of imines to carbonyl compounds.

A cispentacin derivative was synthesized asymmetrically using an enantioselective technique. Since the substrate is an achiral imino-ester, it lacks a chiral auxiliary group to guide the stereochemical reaction as well as a chiral center of its own. It was created in situ (inside the reaction mixture) because the imine substrate was unstable. The racemic β- lactam was then produced in a 30% yield by an enolate- imine cyclization process. This yield implies that optimal product production was not achieved by optimizing the reaction conditions.[10]

Scheme 4

Synthesis of Azetidine-2-one derivatives from pyrazine-2-amino.

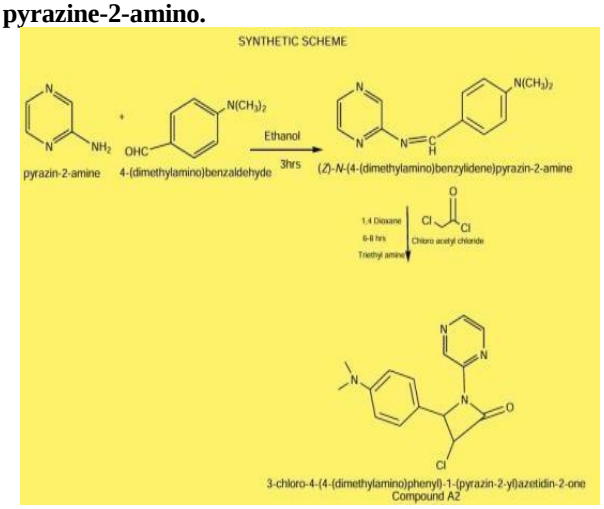


Fig. 8: Synthesis of Azetidine-2-one derivatives from pyrazine-2-amino.

The reaction in the synthesis involves the transformation of a Schiff base, specifically Z- N- 4-dimethylaminobenzylidenepyrimidine-2- amine, with chloroacetyl chloride in the presence of triethylamine and dioxane as solvent. This is a classic example of a heterocyclic cyclization where the imine (Schiff base) acts as a nucleophile and attacks the electrophilic carbonyl carbon of chloroacetyl chloride. The lone pair on the nitrogen of the Schiff base attacks the carbonyl carbon of chloroacetyl chloride. This nucleophilic addition triggers a (2+2) cycloaddition, forming a four-membered azetidinone ring. Triethylamine acts as a base, neutralizing the HCl produced and facilitating ring closure. The final product is the azetidine-2-one derivative, purified by standard filtration, washing, and recrystallization. This reaction is significant in medicinal chemistry as the β-lactam (azetidinone) ring is present in antibiotics like penicillins and cephalosporins, contributing to their biological activity. The described methodology allows for the efficient creation of novel azetidinone derivatives for further pharmacological evaluation.[11]

Scheme 5

The synthesis of azetidine by multicomponent reaction (MCR)

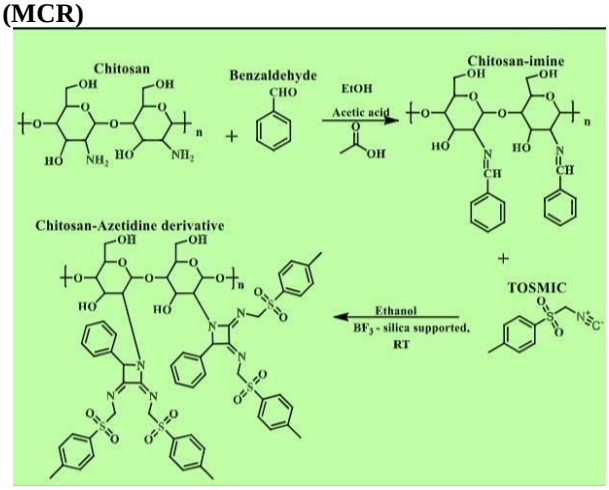


Fig. 9: The synthesis of azetidine by multicomponent reaction (MCR).

The synthesis of azetidine by multicomponent reaction (MCR). A new chitosan-azetidine derivative was synthesized using a one-pot multicomponent reaction (MCR) approach.To understand the mechanism of action, the study employed Scanning Electron Microscopy (SEM) and confocal microscopy. The synthesis of the novel chitosan-azetidine derivative was accomplished using a one-pot multicomponent reaction (MCR) methodology, specifically an ABB approach. The synthesis of azetidine by multicomponent reaction (MCR).[12]

Scheme 6

The synthesis of azetidine derivative from1-Phenylhydrazine.

Substituted aldehyde: NM1= Benzaldehyde, NM2= P Chloro benzaldehyde, NM3= 3- Nitrobenzaldehyde, NM4= Diamino benzaldehyde, NM5= 4-Bromo benzaldehyde and NM6= 2-Chlorobenzaldehyde.

Synthesis of 1-substituted-5- phenylthiocarbohydrat

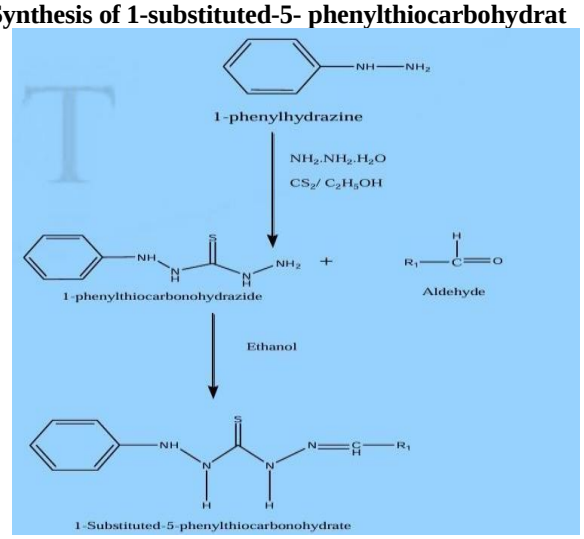


Fig. 10: The Synthesis of 1-substituted-5-phenylthiocarbohydrate.

Synthesis of 4-(3-chloro-2oxo-4- substitutedazetidine 1-yl)-1-pheny thio semi carbazide.

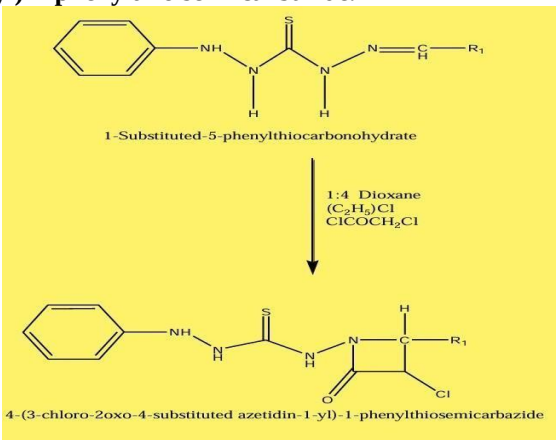


Fig. 11: Synthesisof4-(3-chloro-2oxo-Substituted azetidine 1-yl)-1-phenylthiosemicarbazide.

A solid which is obtained by compound B (0.1mole) is added in the chloroacetyl chloride (0.1mole) in the presence of Et2N was dissolved in acetone at room temperature and allow to reaction. The reaction mixture was first continuously stirred on a magnetic stirrer for about 2-3hr in the ice bath. Then kept it overnight and make it in a powder form in the presence of Ethanol and filter it.[13]

Scheme 7

Synthesis of azetidine ring from Novel Schiff Base Derived Quinoline.

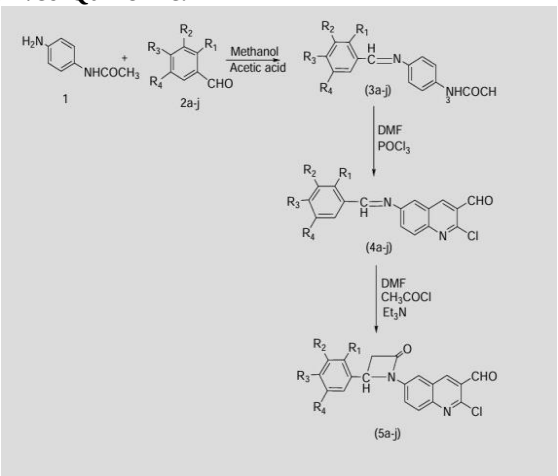


Fig. 12: Synthesis of azetidine ring fromNovel Schiff Base Derived Quinoline.

The mixture of 4- amine acetanilide 1 (0.1m) and 4-methaoxy benzaldehyde (0.1m) was dissolved in methanol (30 mL), these solution was acidified by adding glacial acetic acid (2-3 drops) and reflux for 5h. The excess of solvent was removed under reduced pressure. The resulting compound 3a was washed with solvent ether, dried and crystallized from ethanol. Preparation of 6-(4-methoxybenzylideneamino) chloroquinoline-3-carbaldehyde 4a 2 To the ice- cold dimethyl formamide (0.3 m), phosphoric chloride (0.7 m) was added drop wise with constant stirring and after one hour in this The reaction mixture was heated 17 h at 900C. The reaction was monitor by TLC, after completion the reaction mixture poured in ice cold water. and crystallized from ethyl acetated and methanol (1:1).[14]

Pharmacological activity

Anti-malarial activity Micah Maetani et al, (2016) indentified Antimalarial activity of Azetidine-2-carbonitriles.

That Block P.falciparum Dihydroorotate Dehydrogenase. The identification and enhancement of a novel series of antimalarial agents, azetidine-2- carbonitriles, that block the activity of the P. falciparum dihydroorotate dehydrogenase (DHODH) enzyme.

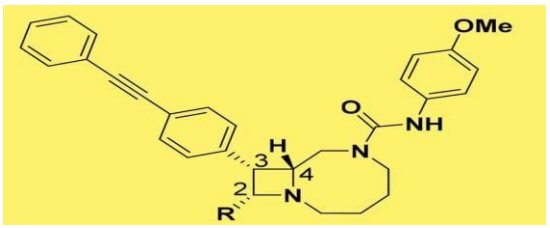


Fig.13 Azetidine-2-carbonitriles

Since these parasites do not possess salvage pathways for pyrimidine production, blocking this de novo synthesis route is an established approach for developing antimalarial medications, found via a high-throughput screening of a library developed through diversity-oriented synthesis (DOS). Demonstrated strong effectiveness against the multidrug-resistant Dd2 strain of P. falciparumand preferentially targeted the parasite's DHODH enzyme rather than the human counterpart.[21]

Anticancer Agents Fabian E Olazaran et al, introduced the potential effect on the anticancer of azetidine derivative. This research evaluates the potential anticancer activity of sixteen synthetically produced azetidin-2-one derivatives. These compounds were categorized into three series: N-(4- methoxyphenyl)-3-phenoxy azetidin-2-one, N-(4-methoxy- phenyl)-3-methoxy-azetidin-2- one, and N-(1,3- benzothiazol)-3phenoxy- azetidin-2-one. The study assessed their cytotoxic effects on SiHa (cervical cancer) and (murine melanoma) cancer cell lines, as well as on non-cancerous Chang liver cells. identified as N-(p-methoxy-phenyl)- 2-(p-methyl-phenyl)-3- phenoxy-azetidin-2-one, demonstrated significant cytotoxic activity against both cancer cell lines while showing considerably lower toxicity towards the healthy Chang cells, indicating high selectivity for neoplastic cells.[22]

Anti-fungal Agents

Mrunmayee P. Toraskar, Vilasrao J. Kadam, Vithal M. Kulkarni (2009) studied the azetidinone derivatives as anti-fungal agent, Fungal infections, particularly those caused by Candida albicans, are a growing concern in immunocompromised patients. Existing antifungal

agents, such as azoles (fluconazole, itraconazole), act primarily through inhibition of fungal cytochrome P-450 (CYP-450) enzymes.

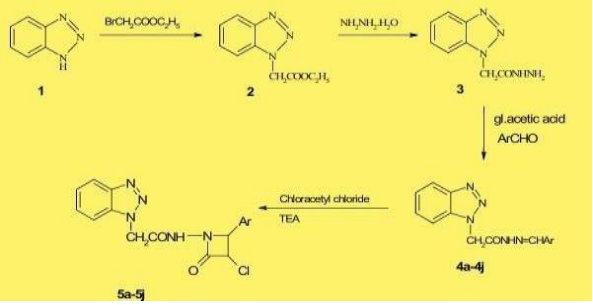


Fig. 14: Azetidinone derivatives.

Involved in ergosterol biosynthesis, an essential component of the fungal cell membrane. However, resistance and side effects limit their effectiveness. To address these issues, researchers have explored novel heterocyclic scaffolds.

Among them, azetidinones (β-lactams) are known for diverse a various pharmacological properties (antibacterial, antifungal, anti-inflammatory, antitubercular). Similarly, benzotriazole derivatives are well established as antimicrobial and anticancer agents. Combining these two moieties into a single molecular framework provides an opportunity to design new antifungal candidates study highlights these molecules as potential antifungal leads with structural features (lipophilicity, electron- donating substituents) directly influencing their activity. Docking studies further support their mechanism as CYP-450 inhibitors, providing a strong pharmacological basis for further development.[23]

Anti-Inflammatory Agents This research examines the in vivo biological assessment of six novel azetidine-2-one derivatives of ferulic acid, referred to as 6a–f. After assessing toxicity, the derivatives were tested for their anti- inflammatory capabilities using two rat models: an acute inflammation model triggered by carrageenan and a chronic inflammation model through a granuloma test. In the acute model, all compounds reached peak effectiveness at 24 hours, indicating they are long-lasting, with compound 6b displaying the strongest activity, similar to standard medications such as diclofenac and indomethacin. In the chronic model, all derivatives successfully diminished the creation of granulation tissue, with compound 6b once more demonstrating a notable inhibitory effect (76.02%) similar to that of indomethacin. The research finds that the novel azetidine-2-one derivatives of ferulic acid, particularly compound 6b (featuring a 4-Fluoro substituent), show potential as anti- inflammatory agents with an improved toxicological profile compared to diclofenac.[26]

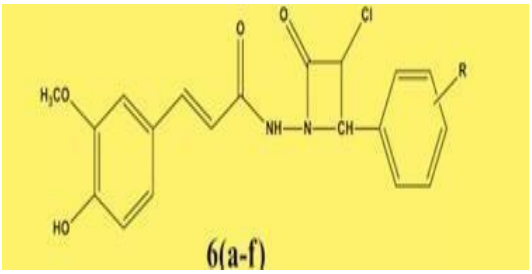


Fig. 15: Azetidine derivative of ferulic acid.

Anti-Diabetic and Renoprotective Activity The compounds 2-((1,3-Diphenyl-1'H-pyrazol- 4-yl) methylidene- hydrazine acetyl mercapto benzimidazole and 2-((1,3-Diphenyl-1'H- pyrazol-4-yl) methylidene hydrazine acetyl were tested. Both compounds effectively restored serum glucose levels to normal, comparable to the reference medication gliclazide.

Heterocyclic structures with the pyrazole core are beneficial for controlling hyperglycemia and associated dyslipidemia.[25]

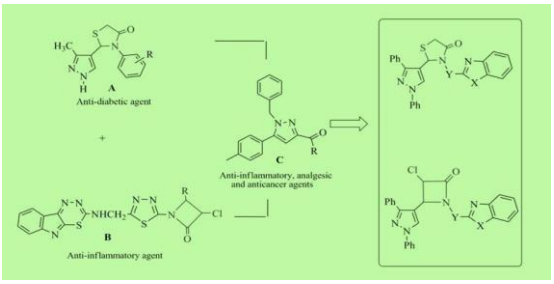


Fig. 16: Azetidine-2-one derivative

Azetidine containing dipeptides as HCMV inhibitors [antiviral drug]

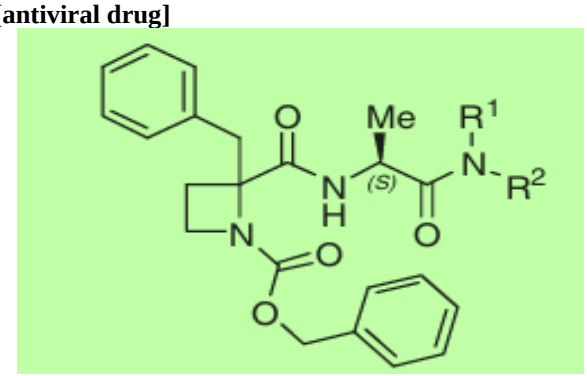


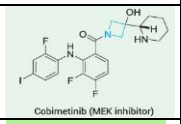
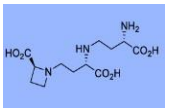
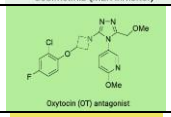
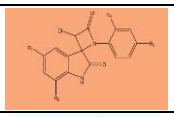
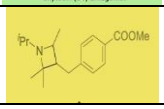
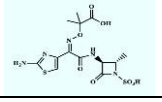
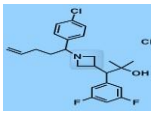
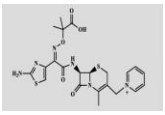
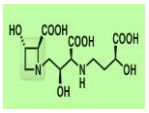
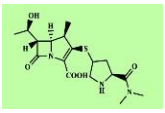
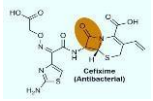
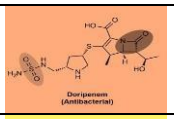
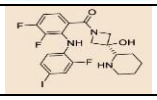
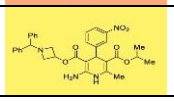
Fig. 17: Azetidine containing dipeptides.

Paula Perez-Faginas et al. conducted a study on the antiviral activity of azetidine- containing dipeptides. This research investigates the structure–activity relationship (SAR) of dipeptide inhibitors containing azetidine that target human cytomegalovirus (HCMV). The researchers synthesized three sets of modified analogues by altering the N- terminus, C- terminus, and C-terminal side chain of a prototype compound. The antiviral assays revealed that specific structural features were critical for efficacy: a non-substituted C- carboxamide or aliphatic group, an aliphatic C- terminal side chain, and a

benzyloxycarbonyl group at the amino terminus. These structural components were essential for maintaining anti-HCMV properties. The azetidine component contributed conformational rigidity to the dipeptide, resulting in a γ-type reverse turn, as confirmed by ^{1}H NMR studies, which likely enhanced antiviral activity.[24]

Derivatives of Azetidine

Table 1: Contains various Derivatives of Azetidine.

No	structure	Name	Activity	No	Structure	Name	Activity
1		Cobimetinib [15]	Mek inhibitor	8		Nicotianamie[18]	Metal detoxification
2		Oxytocin [15]	oxytocin receptor.	9		spiro[azetidine-2,30- indole]-2,4(10H)-dion[19]	Antiviral
3		Isopropyl-amino dimethyl-azetidine-benzoate [15]	Antibacterial, antiviral agent.	10		Aztreonam [20]	Antibacterial
4		Amino-2-(3-hydroxy-1-adamantyl)-acetyla Zabicyclo-hexane carbonitrile[16]	DPP-4 inhibitor	11		Ceftazidime[20]	Anti-bacterial
5		2-oxo-hexahydr1H thieno[3,4d]imidaz ol-4- yl]pentanoic acid [16]	Antifungal	12		Meropenem[20]	Anti-bacterial
6		Cefixime [17]	Antibacterl	13		Doripenam[17]	Anti-bacterial
7		Cobimetinib [18]	Anticancer	14		Azelnidipine [18]	Anti-hypertension

CONCLUSION

Azetidine and its derivatives form a unique class of heterocycles valued for their ring strain, synthetic versatility, and wide pharmacological potential. Advancements in cyclization, cycloaddition, metal-catalyzed, multicomponent, and ring-expansion methods have enabled efficient synthesis of diverse azetidine scaffolds for biological evaluation.Their derivatives show strong therapeutic potential as antibacterial, antifungal, antioxidant, anti- inflammatory, anti-diabetic, renoprotective, and antimalarial agents. Structural modifications, particularly with electron-withdrawing groups or hybridization with other heterocycles, significantly enhance their bioactivity. The azetidin-2-one core remains especially notable for its potent biological properties.Emerging synthetic technologies such as photoredox catalysis, flow chemistry, and diversity- oriented synthesis are driving innovation, though challenges persist in selectivity, pharmacokinetics, and toxicity. Future progress depends on integrating computational modeling, structure–activity studies, and in vivo experiments through multidisciplinary collaboration to fully realize azetidine's therapeutic promise.

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