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REVIEW ARTICLE

A Review on Chemistry, Synthesis and Uses of Thiazolidin-4-ones

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Abstract: Thiazolidin-4-ones are prominent heterocyclic scaffolds that continue to attract considerable attention in the field of medicinal chemistry due to its broad and potent pharmacological activities. This nucleus is a versatile pharmacophore, and its derivatives have demonstrated a wide array of therapeutic effects, including antimicrobial, anticancer, anti-inflammatory, and antidiabetic properties. The structural flexibility of the thiazolidin-4-one ring allows for substitutions at various positions, enabling the modulation of its biological profile and the development of compounds with enhanced potency and selectivity. Key structure-activity relationship studies have revealed that modifications at the C-2, N-3, and C-5 positions significantly influence the pharmacological outcomes. For instance, the introduction of bulky aromatic or heterocyclic moieties at the C-2 and N-3 positions has often been correlated with increased antimicrobial and anticancer efficacy. Similarly, the functionalization of the C-5 position, frequently with an arylidene group, has been shown to be critical for anti-inflammatory and enzyme inhibitory activities. This document provides a detailed account of the synthetic methodologies developed for thiazolidin-4-one derivatives, from classical multi-component reactions to modern catalytic approaches. It further delineates the extensive spectrum of their biological applications, offering insights into their mechanisms of action and therapeutic potential. This scaffold promises the discovery of novel drug candidates to address a variety of human diseases.

Keywords: Thiazolidin-4-ones; Heterocyclic Chemistry; Medicinal Chemistry; Structure-Activity Relationship; Drug Discovery

1. Introduction

Heterocyclic compounds form the cornerstone of modern medicinal chemistry, with a vast majority of pharmaceuticals containing at least one heterocyclic ring system. Their structural diversity and ability to interact with biological macromolecules make them indispensable scaffolds in drug design and development [1]. Among the myriad of heterocyclic structures, those incorporating nitrogen and sulfur atoms have proven to be particularly fruitful sources of bioactive molecules. The thiazole nucleus and its saturated analogue, thiazolidine, are prominent examples of such pharmacologically significant heterocycles.

The thiazolidin-4-one core, a derivative of thiazolidine featuring a carbonyl group at the fourth position, has emerged as a "privileged scaffold" in medicinal chemistry. Its discovery within the structure of penicillin marked a pivotal moment, unveiling the therapeutic potential of this five-membered ring system [2]. The unique structural features of the 1,3-thiazolidin-4-one ring, including the presence of a sulfur atom, a nitrogen atom, and a carbonyl group, provide multiple sites for functionalization, allowing for the generation of extensive chemical libraries for biological screening. The stereochemistry at the C-2 and C-5 positions further adds to its structural diversity.

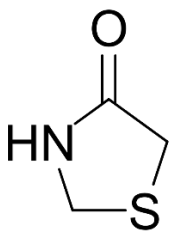

Figure 1. Thiazolidin-4-one Structure

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The uniqueness of the thiazolidin-4-one scaffold is reflected in the broad spectrum of biological activities exhibited by its derivatives. These compounds have been reported to possess antimicrobial, antitubercular, antiviral, anticancer, anti-inflammatory, and antidiabetic properties, among others [3, 4]. The mechanism of action often involves the inhibition of specific enzymes or the modulation of cellular signaling pathways. For example, some thiazolidin-4-one derivatives have been shown to inhibit bacterial enzymes like MurB, which is crucial for peptidoglycan biosynthesis, thereby exerting their antibacterial effect [5]. The sustained interest in this heterocyclic system stems from the potential to fine-tune its biological activity through rational chemical modifications, leading to the development of novel therapeutic agents with improved efficacy and reduced toxicity. This review aims to provide an overview of the synthetic techniques employed for the construction of the thiazolidin-4-one ring and to detail the diverse pharmacological applications of its derivatives, highlighting the main structure-activity relationships.

2. Synthesis of Thiazolidin-4-ones

The construction of the thiazolidin-4-one scaffold has been a subject of extensive research, leading to the development of various synthetic routes. The most prevalent methods are multi-component reactions, which offer the advantage of efficiency and atom economy by combining three or more reactants in a single step.

2.1. Three-Component Condensation Reactions

The classical and most widely employed synthesis of 2,3-disubstituted-1,3-thiazolidin-4-ones involves the one-pot condensation of an amine, a carbonyl compound (aldehyde or ketone), and a mercapto-carboxylic acid, typically mercaptoacetic acid (thioglycolic acid) [6]. The reaction proceeds through the initial formation of a Schiff base (imine) from the amine and the carbonyl compound, which then undergoes a nucleophilic attack by the thiol group of the mercaptoacetic acid, followed by an intramolecular cyclization via amide bond formation with the elimination of a water molecule.

Table 1. Synthetic Methods for Thiazolidin-4-one Derivatives.

Synthesis Method	Reactants	Catalysts/Reagents	Conditions	Features	Reference
Three-Component Condensation	Amine, Carbonyl Compound, Mercaptoacetic Acid	Toluene, Benzene (Azeotropic)	Reflux	One-pot, high atom economy, classical method.	[6]
Solvent-Free Condensation	Quinolinyl Azomethines, Mercaptoacetic Acid	Silica Chloride	Solvent-free, mild conditions	Environmentally friendly, heterogeneous catalysis.	[7]
Synthesis from Thiourea	Thiourea, α-Haloacetic Acid (e.g., Chloroacetic Acid)	Sodium Acetate, Ethanol	Reflux	Provides access to 2-imino-thiazolidin-4-ones.	[9]
Microwave-Assisted Synthesis	Thiosemicarbazone, Maleic Anhydride	Microwave Irradiation	Rapid, high yield	Significantly reduced reaction times and improved efficiency.	[11]
Heterogeneous Catalysis	Isatin, α-Mercaptopropionic Acid, 3-Amino-5-methylisoxazole	nano-TiO_2-SO_3H	Solvent-free, 80 °C	Reusable catalyst, suitable for spiro-heterocycle synthesis.	[12]

This reaction can be performed under various conditions, often employing azeotropic distillation with solvents like benzene or toluene to remove water and drive the reaction to completion. Catalysts such as silica chloride have been used to facilitate the reaction under solvent-free conditions, promoting a more environmentally friendly approach [7].

2.2. Reactions of Schiff Bases with Mercaptoacetic Acid

A two-step variation of the three-component synthesis involves the pre-formation and isolation of the Schiff base, which is then reacted with mercaptoacetic acid. This method allows for better control over the reaction and purification of the intermediate. Bolognese et al. reported the synthesis of various 1,3-thiazolidin-4-one derivatives by reacting benzylidene-anilines with mercaptoacetic acid in benzene, achieving good yields after chromatographic purification [8].

2.3. Synthesis from Thiourea Derivatives

Thiourea and its derivatives serve as versatile starting materials for the synthesis of various thiazolidin-4-one analogues. For instance, 2-imino-1,3-thiazolidin-4-ones can be prepared by the reaction of thiourea with α-halo acids or their esters, such as chloroacetic acid or ethyl bromoacetate, in the presence of a base like sodium acetate [9]. The reaction involves the initial S-alkylation of thiourea followed by intramolecular cyclization.

Further modifications, such as Knoevenagel condensation of the resulting 2-imino-1,3-thiazolidin-4-one with various aldehydes at the C-5 position, can introduce additional diversity to the scaffold, leading to compounds with potent biological activities [10].

2.4. Other Synthetic Methods

Several other innovative methods have been developed for the synthesis of thiazolidin-4-ones. Microwave-assisted organic synthesis (MAOS) has been successfully applied to accelerate the reaction rates and improve yields. For example, the synthesis of 2-hydrazono-4-thiazolidinones has been achieved through a microwave-irradiated reaction of thiosemicarbazones with maleic anhydride [11].

Catalytic methods have also been explored. Ruby Singh et al. developed a solvent-free synthesis of isoxazolyl-spiro-thiazolidinones using a nano-titania-supported sulfonic acid catalyst, highlighting the potential of heterogeneous catalysis in the synthesis of these heterocycles [12].

3. Pharmacology of Thiazolidin-4-one Derivatives

The thiazolidin-4-one scaffold is associated with a remarkable diversity of biological activities, making it a focal point of research in drug discovery.

3.1. Antimicrobial and Antifungal Activity

The emergence of multidrug-resistant microbial strains has created an urgent need for the development of novel antimicrobial agents. Thiazolidin-4-one derivatives have shown significant promise in this area. Their antibacterial activity is often attributed to the inhibition of essential bacterial enzymes.

Structure-activity relationship (SAR) studies have indicated that the nature of the substituents at the C-2 and N-3 positions of the thiazolidin-4-one ring is crucial for antimicrobial potency [13]. For example, compounds bearing an antipyrine moiety at N-3 and a 3-iodo substituted phenyl ring at C-2 have demonstrated strong activity against both Gram-positive and Gram-negative bacteria [14]. Furthermore, the introduction of other heterocyclic rings, such as pyrimidine or imidazole, to the thiazolidin-4-one core has been shown to enhance antibacterial and antifungal effects [15, 16].

Table 2. Thiazolidin-4-one Derivatives with Antimicrobial Activity.

Compound Structure/Description	Substituents	Target Organisms	Activity/Observations	Reference
2-(3-Iodophenyl)-3-(antipyrinyl)-thiazolidin-4-one	C-2: 3-Iodophenyl N-3: Antipyrine	*E. coli*, *B. subtilis*, *S. typhi*	Showed significant zones of inhibition against tested strains.	[14]
2-Thioxo-4-thiazolidinones with pyrimidine and sulfamoyl moieties	Core: 2-Thioxo-4-thiazolidinone Substituents: Pyrimidine, Sulfamoyl Phenyl, Thienyl	*B. cereus*, *S. aureus*	Exhibited moderate to high antibacterial activity.	[15]
Thiazolidinones from 5-methyl-1-H-imidazole-4-carboxylate	Core: Imidazole-Thiazolidinone hybrid	*B. subtilis*, Fungi	Displayed modest antibacterial and antifungal properties.	[16]
N-[(2Z)-3-(4-bromophenyl)-4-oxo-1,3-thiazolidin-2-ylidene]-2-(pyrazin-2-yloxy)	Core: Pyrazine-Thiazolidinone hybrid Substituent: 4-Bromophenyl	*E. coli*, *S. typhi*, *S. aureus*, *B. subtilis*	Showed broad-spectrum antibacterial activity.	[16]

3.2. Antitubercular Activity

Tuberculosis remains a major global health problem, and the development of new drugs to combat resistant strains of *Mycobacterium tuberculosis* is a priority. Several thiazolidin-4-one derivatives have been evaluated for their antimycobacterial activity. Compounds with a furan or a fluorinated phenyl group at the C-2 position have shown significant inhibition of mycobacterial growth [17]. The structural analysis of N-pyridyl-N'-thiazolyl hydrazine derivatives revealed that the presence of 2-pyridyl and 2-hydroxy-5-methoxyphenyl groups is beneficial for antitubercular activity [18].

3.3. Anticancer Activity

The search for novel anticancer agents is a continuous effort in medicinal chemistry, and thiazolidin-4-one derivatives have emerged as a promising class of compounds with cytotoxic and antiproliferative properties. Their mechanisms of action are varied and can include the induction of apoptosis, cell cycle arrest, and inhibition of key enzymes involved in cancer progression.

Table 3. Selected Thiazolidin-4-one Derivatives with Notable Anticancer Activity.

Compound Structure/Description	Substituents	Cancer Cell Lines	Activity/Mechanism of Action	Reference
2-Arylthiazolidine-4-carboxylic acid amides	C-2: 4-(Acetamido)phenyl Amide: $C_{18}H_{37}$ alkyl chain	PPC-1 (Prostate)	Potent and selective cytotoxicity (IC_{50} = 0.55 μM). Potency increases with alkyl chain length.	[19]
2-Aryl-4-oxo-thiazolidin-3-yl-amides	N-3: Amide linkage to a $C_{18}H_{37}$ alkyl chain	Human Prostate Cancer	Antiproliferative activity increased with longer alkyl chains.	[20]
5-Bromo-3-[(hydrazono)]-1H-2-indolinones	Core: Indolinone-Thiazolidinone hybrid Substituent: C-5 Bromo	NCI-H460, MCF7, SF-268	Demonstrated potential cytotoxic properties.	[21]
6-Aminoflavone-Thiazolidinone hybrids	Core: Flavone-Thiazolidinone hybrid	Dalton's Ascites Carcinoma (in vivo)	Enhanced lifespan, prevented body weight increase, induced apoptosis.	[22]

A series of 2-arylthiazolidine-4-carboxylic acid amides were found to be potent and selective cytotoxic agents against prostate cancer cells, with the length of the alkyl chain in the amide moiety being a critical determinant of activity [19]. Similarly, 2-aryl-4-oxo-thiazolidin-3-yl amides have shown significant antiproliferative effects [20]. Other derivatives, such as those incorporating indolinone or coumarin moieties, have also demonstrated promising anticancer potential through various mechanisms, including apoptosis induction [21, 22].

3.4. Anti-inflammatory and Analgesic Activity

Inflammation is a complex biological response implicated in numerous diseases. Thiazolidin-4-one derivatives have been investigated for their anti-inflammatory properties, often targeting cyclooxygenase (COX) enzymes. By designing molecules that selectively inhibit the COX-2 isoform, it is possible to achieve anti-inflammatory effects with reduced gastrointestinal side effects compared to non-selective NSAIDs.

Quinazolinone-thiazolidinone hybrids have shown anti-inflammatory activity comparable to the standard drug phenylbutazone [23]. Biphenyl-4-carboxylic acid derivatives of 5-(arylidene)-2-(aryl)-4-oxothiazolidin-3-yl amide also exhibited significant anti-inflammatory effects, with halogen substitutions on the aromatic rings enhancing the activity [24]. These results suggest that the thiazolidin-4-one scaffold can serve as a template for the development of new anti-inflammatory and analgesic agents.

3.5. Antidiabetic Activity

Perhaps the most clinically significant application of the thiazolidinone core is in the management of type 2 diabetes mellitus. The thiazolidinedione (TZD) class of drugs, also known as "glitazones," which includes compounds like Pioglitazone and Rosiglitazone, are based on a 2,4-thiazolidinedione scaffold [25]. These agents act as potent and selective agonists of the peroxisome proliferator-activated receptor gamma (PPARγ), a nuclear receptor that plays a central role in regulating glucose and lipid metabolism. Activation of PPARγ enhances insulin sensitivity in adipose tissue, skeletal muscle, and the liver, leading to improved glycemic control [26]. Despite their efficacy, the use of first-generation TZDs has been associated with adverse effects such as fluid retention, weight gain, and cardiovascular concerns, which has prompted extensive research into developing newer generations of thiazolidinone-based antidiabetic agents with improved safety profiles.

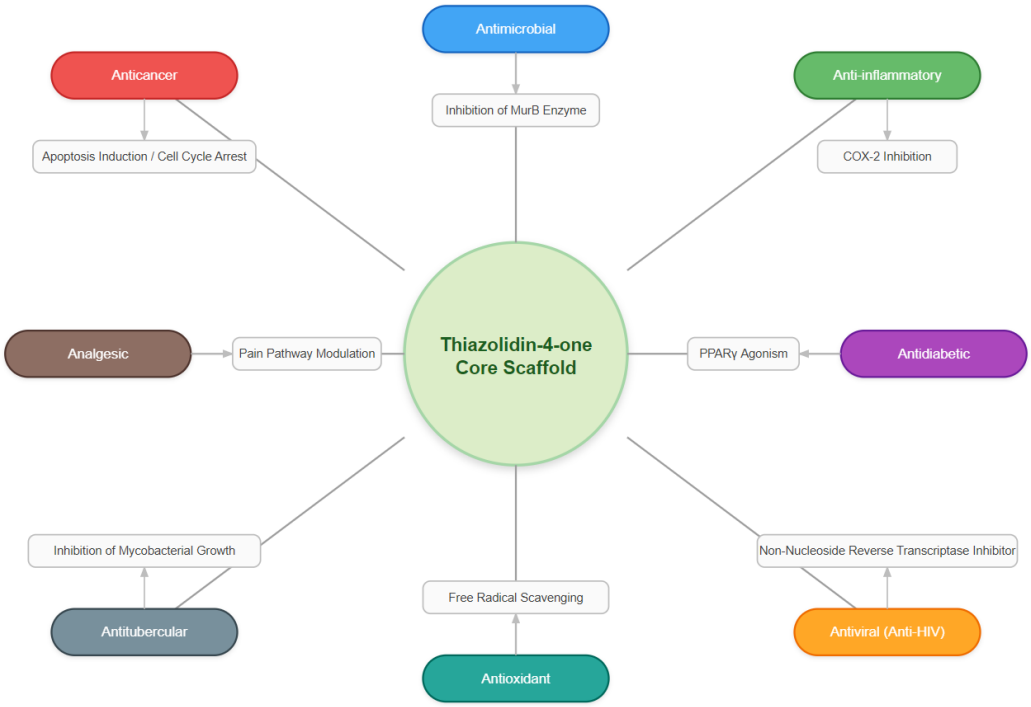

Figure 2. Pharmacology of Thiazolidin-4-ones

Table 4. Thiazolidin-4-one Derivatives with Anti-inflammatory Activity

Compound Structure/Description	Substituents	Assay/Model	Activity/Observations	Reference
Quinazolinone-Thiazolidinone hybrids	C-2: 4-Chlorophenyl Core: 6-Bromo-quinazolinone	Carrageenan-induced paw edema (rats)	Anti-inflammatory effect was nearly identical to the standard drug phenylbutazone.	[23]
Biphenyl-4-carboxylic acid 5-(arylidene)-2-(aryl)-4-oxothiazolidin-3-ylamides	Substituents: Bromine on both C-2 and C-5 aryl rings	Carrageenan-induced paw edema (rats)	Significant inhibition of edema (55.73% at 4 hours).	[24]
3,3'-(1,2-Ethanediyl)-bis[2-aryl-4-thiazolidinone] derivatives	Dimeric structure with aryl groups	In vivo analgesic/anti-inflammatory tests	Showed remarkable stereoselective anti-inflammatory and analgesic actions, likely via COX-2.	[32]
Thiadiazolyl-thiazolidinone hybrids	Core: Indole-Thiadiazole-Thiazolidinone hybrid	Carrageenan-induced paw edema (rats)	Exhibited potent anti-inflammatory activity.	[33]

3.6. Antiviral Activity

The thiazolidin-4-one nucleus has also been explored for its potential as an antiviral agent, particularly against the human immunodeficiency virus (HIV). Several derivatives have been identified as non-nucleoside reverse transcriptase inhibitors (NNRTIs). These compounds bind to an allosteric site on the HIV-1 reverse transcriptase enzyme, inducing a conformational change that inhibits its catalytic activity and prevents the conversion of viral RNA into DNA [27]. Structure-activity relationship studies have demonstrated that the presence of specific aryl and heteroaryl groups at the C-2 and N-3 positions of the thiazolidin-4-one ring is critical for potent anti-HIV activity. The scaffold's ability to be readily modified allows for the optimization of its interactions within the NNRTI binding pocket, making it a valuable template for the design of novel antiviral drugs [28].

3.7. Antioxidant Activity

Oxidative stress, resulting from an imbalance between the production of reactive oxygen species (ROS) and the body's ability to neutralize them, is implicated in the pathogenesis of numerous diseases, including cancer, neurodegenerative disorders, and cardiovascular conditions. Thiazolidin-4-one derivatives have been investigated for their antioxidant properties and their capacity to act as free radical scavengers. The antioxidant activity is often linked to the presence of specific structural motifs, such as phenolic

hydroxyl groups attached to an aryl substituent [29]. These groups can donate a hydrogen atom to neutralize free radicals. Furthermore, the arylidene moiety at the C-5 position can enhance antioxidant capacity through resonance stabilization of the resulting radical. The evaluation of these compounds in assays such as the DPPH (2,2-diphenyl-1-picrylhydrazyl) radical scavenging assay has confirmed the potential of the thiazolidin-4-one scaffold in developing agents to combat oxidative stress [30].

Table 5. Thiazolidin-4-one Derivatives with Antidiabetic, Antiviral, and Antioxidant Activities.

Biological Activity	Compound Class/Description	Mechanism of Action / Target	Structural Features	Reference(s)
Antidiabetic	Thiazolidinediones (TZDs), e.g., Pioglitazone, Rosiglitazone	PPARγ (Peroxisome Proliferator-Activated Receptor gamma) Agonist	2,4-Dione substitution on the thiazolidine ring.	[25, 26]
Antiviral (Anti-HIV)	2-Aryl-3-heteroaryl-1,3-thiazolidin-4-ones	Non-Nucleoside Reverse Transcriptase Inhibitor (NNRTI)	Specific aryl and heteroaryl groups at C-2 and N-3 positions are critical.	[27, 28]
Antioxidant	5-Arylidene-thiazolidin-4-ones	Free Radical Scavenging	Phenolic hydroxyl groups on aryl rings; Arylidene moiety at C-5 for resonance stabilization.	[29, 30]

4. Conclusion

The thiazolidin-4-one ring system continues to be a highly valuable and versatile scaffold in the realm of medicinal chemistry. The ease of its synthesis, primarily through multi-component reactions, and the possibility of introducing a wide range of substituents at various positions, have made it an attractive target for the development of new therapeutic agents. The extensive research conducted on its derivatives has led to the discovery of compounds with a broad spectrum of pharmacological activities, including potent antimicrobial, antitubercular, anticancer, and anti-inflammatory effects. The structure-activity relationship studies have provided valuable insights into the design of more potent and selective thiazolidin-4-one-based drugs. While some derivatives have reached clinical trials, particularly in the area of diabetes, the full therapeutic potential of this scaffold is yet to be realized.

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