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EXPLORING THE THERAPEUTIC POTENTIAL OF 2-AMINOBENZOTHIAZOLE DERIVATIVES IN CANCER TREATMENT: AN IN-SILICO APPROACH

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ABSTRACT

Cancer remains prevalent for the significant healthcare concern worldwide urging the development of efficient, selective and less toxic anticancer agents. The benzothiazole nucleus, particularly 2-Aminobenzothiazole having a heterocyclic structure with sulfur and nitrogen atom, has been investigated widely due to its broad spectrum of pharmacological activities including anticancer, antimicrobial, anti-inflammatory and other properties. This article reviews the anticancer potential of benzothiazole scaffold encompassing the chemical structure, structural activity relationship from different derivatives. Various synthesis methods and the pharmacological properties exhibited by the benzothiazole derivatives with special emphasis on anticancer activity are extensively reviewed.

KEYWORDS: 2-Aminobenzothiazole, Anticancer, Benzothiazole.

INTRODUCTION

Cancer, characterized by the uncontrolled and aggressive proliferation of abnormal cells, is one of the deadliest diseases in the world.[1] Cancer is a mass of cells with malignant

transformation, which divide uncontrollably, invade and spread to distant organs, and develop secondary disease. Cancer is among the four major non communicable disease (heart disease, cancers, lung disease and diabetes) that are the leading causes of deaths worldwide.[2]

Heterocycles are important pharmacophores and have significance to create privileged chemical structures possessing pharmacological activities.[3] Benzothiazole plays an important role in the field of medicinal chemistry and renders an extensive range of biological activities including anti-cancer, anti-bacterial, anti-tuberculosis, anti-diabetic, anthelmintic, anti-tumour, anti-viral, anti-oxidant, anti-inflammatory, anti-glutamate and anti-parkinsonism, anticonvulsant, muscle relaxant activities, neuroprotective, and inhibitors of several enzymes.[4] Benzothiazole derivatives exhibit remarkable and prevalent biological and pharmacological activities against different types of tumours and cancer cell lines.[3] Nitrogen/sulfur containing heterocycles are biologically important scaffolds, and they are widely present in a number of natural products and commercially available drugs.[1] 2-aminobenzothiazole stands as a prominently featured scaffold in medicinal chemistry, prevalent in bioactive molecules, particularly those pertaining to cancer agents. 2-aminobenzothiazole derivatives have emerged as novel antineoplastic agents, showcasing a diverse range of protein targets, including tyrosine kinases such as EGFR, CSF1R, VEGFR-2, MET, and FAK, serine/ threonine kinases such as Aurora, CK, CDK, DYRK2, and RAF, mutant p53protein, BCL-XL, PI3K kinase, HSP90, NSD1, HDAC, LSD1, DNA topoisomerases, FTO, mPGES-1, hCA IX/XII, SCD, and CXCR receptor.[5] Ongoing research continues to explore the potential applications and properties of benzothiazole compounds and their derivatives.[6]

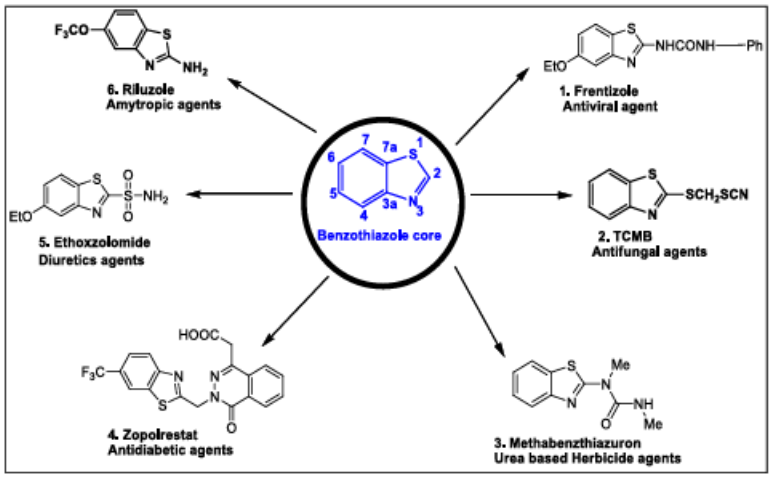


Figure 1: Marketed drugs containing benzothiazole ring.[6]

Table 1: Properties of 2-aminobenzothiazole.

IUPAC NAME	1,3-benzothiazol-2-amine
MOLECULAR FORMULA	$C_7H_6N_2S$
MOLECULAR WEIGHT	150.20 g/mol

2-AMINOBENZOTHIAZOLE CHEMISTRY

Benzothiazole is a heterocycle containing a benzene ring fused to the 4,5-positions of thiazole ring, which exerts a wide range of biological activities.[1] The organic compound 2-aminobenzothiazole has the formula $C_7H_6N_2S$, and its structure can be expressed as a tautomerism of enamines. It is a heterocyclic aromatic amine that consists of a benzene ring fused to a thiazole group, which in turn is attached to an amino group. 2-Aminobenzothiazole's amino group gives it weakly basic properties. 2-Aminobenzothiazole can undergo electrophilic aromatic substitution reactions. These reactions facilitate the molecule's functionalization and the introduction of different groups.[7]

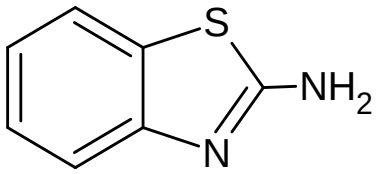


Figure 2: 2ABT.

The amino group of 2-aminobenzothiazole is an active and useful functionality, which could be tethered to many structural fragments or form various fused heterocycles. In addition, the 2-aminobenzothiazole core (exocyclic nitrogen, cyclic sulfur, and cyclic nitrogen) could provide suitable coordination site(s) for metals. Furthermore, 2-aminobenzothiazole acts as a bioisostere for aniline, 2-aminothiazole, 2-aminobenzimidazole, and other nitrogen- or oxygen-containing heterocycles. At the structural level, the 2-aminobenzothiazole fragment can be involved in formation of hydrogen bonds (as a hydrogen bond acceptor and/or donor), chalcogen bonds, as well as π-π stacking/van der Waals contacts with the specific amino acid residues on target proteins, which contribute to inhibitory activity.[1]

SAR

Through systematic alterations of the benzothiazole core and its substituents, researchers can optimize these compounds for enhanced efficacy, selectivity, and reduced toxicity. Substituents on the benzene ring of the benzothiazole core can significantly impact the

compound's activity and pharmacokinetics.[8] The core structural properties of benzothiazole have indicated the significance of a ring structure in the cancer therapies.[6]

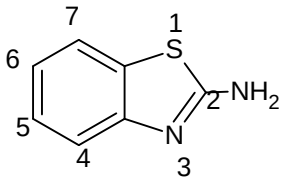


Figure: 3

- The structure should be planar because given significant feature for linkages between the DNA-containing benzothiazole molecules.[6]
- The N-atom must be free and unhindered for the rings of benzothiazole structure to have anticancer activity.[6]
- Electron-donating groups such as hydroxyl (–OH), methoxy ($–OCH_3$), and amino ($–NH_2$) groups typically enhance the electron density of the benzene ring, which can increase binding affinity to certain biological targets.[8]
- Heterocyclic groups such as pyridine, pyrazole, or imidazole can introduce new pharmacophores that enhance the compound's ability to interact with a broader range of biological targets.[8]
- Attaching a pyridine ring to the benzothiazole core can improve aqueous solubility and binding to enzymes or receptors.[8]
- Substitutions at the 6-position with electron-withdrawing groups like nitro (NO2) or electron-donating groups like ethoxy (OEt) have been shown to enhance cytotoxic effects.[1]
- Alkyl chains, on the other hand, can modulate the lipophilicity and membrane permeability of benzothiazole derivatives.[8]
- Substitution of 2-aminobenzothiazole ring with 2-aminothiazole moiety resulted in the loss of anticancer efficacy.[1]
- The MeO group at C-6 was favourable for the antiproliferative activity, whereas Cl atom was detrimental to the activity.[1]
- Replacement of benzothiazole moiety with phenyl, thiazolyl, or oxazolyl group resulted in a drop-in anti-angiogenic activity.[1]
- Incorporating motifs like aminopyridine can significantly boost potency against specific kinases such as CDK2.[1]

GENERAL METHODS OF SYNTHESIS OF 2-SUBSTITUTED BENZOTHIAZOLES

Method 1

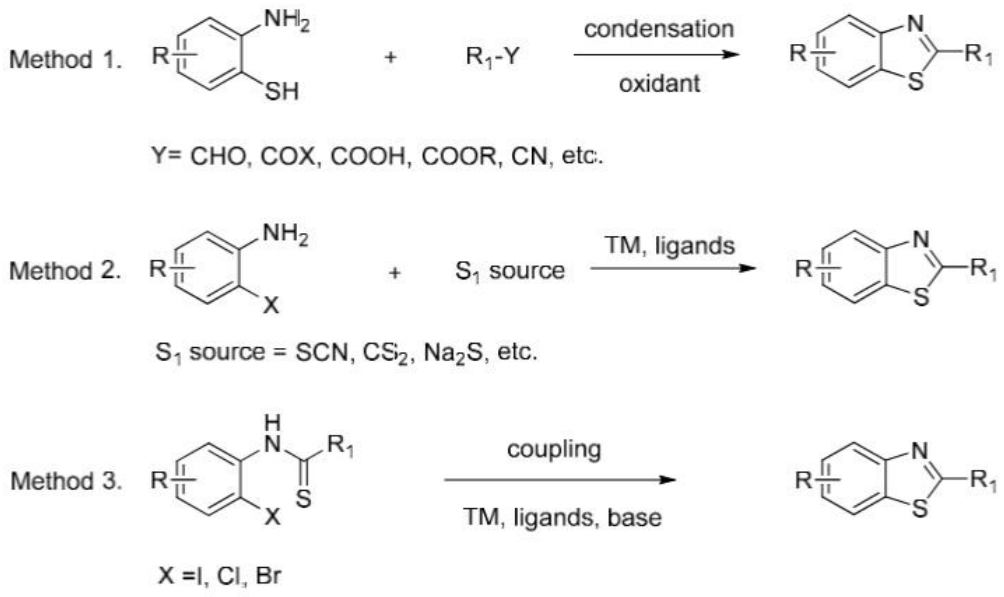
Different synthetic paths have been developed for the preparation of benzothiazole derivatives (Scheme 1). Among them, the condensation reaction of 2-aminobenzenethiol with a carbonyl or cyano group-containing substance is the most commonly used method (Scheme 1, Method 1).[4]

Method 2

Moreover, many researchers found that benzothiazoles could also be synthesized by the reaction of ortho-halogenated aniline with isothiocyanates, carbon disulfide and piperidine, aldehydes and sulfur, carbon disulfide and thiol, acid chloride and Lawesson's reagent (Scheme 1, Method 2).[4]

Method 3

An alternative method is the intramolecular cyclization of ortho-halogenated analogs (Scheme 1, Method 3)[4]

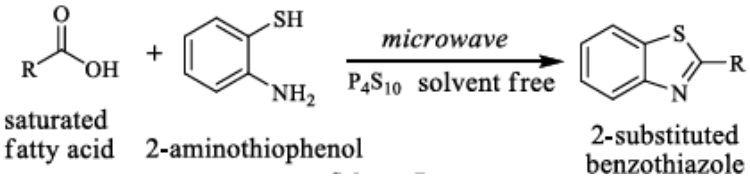


Scheme 1. The common synthetic routes for benzothiazoles.

Method 4

The synthesis of benzothiazoles with 2-substitution was achieved via a thorough condensation reaction using 2-aminothiophenol and olefinic compounds in a solvent-free environment with the assistance of microwave irradiation and using P4S10 as the catalyst

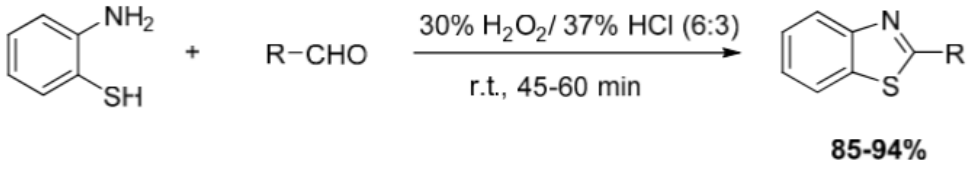
(Scheme 2). This method is highly efficient with a completion time requiring approximately 3–4 min. The use of microwave irradiation and a solvent-free environment contributed to the rapid reaction kinetics. Additionally, the reaction of the desired benzothiazole products in high yields indicated its effectiveness.[6]



Scheme 2

Method 5

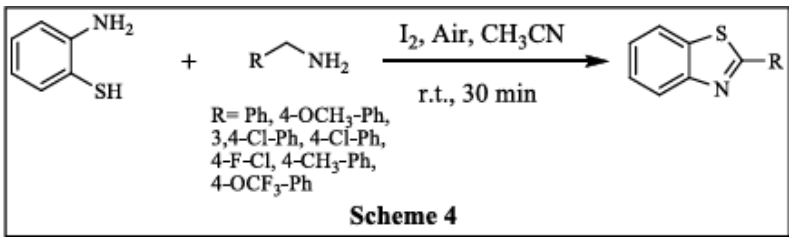
The reaction is catalysed by H2O2/HCl and carried out at room temperature for 1 h. The use of electron-withdrawing aldehydes and electron-donating substituents allows for the synthesis of a diverse range of benzothiazole derivatives with good yields (85–94%) (Scheme 3). One of the advantages of this method is that it is a one-pot reaction which reduces the number of steps required for the synthesis of benzothiazoles. Additionally, the products can be easily separated and the reaction time is relatively short.[6]



Scheme 3. Condensation of 2-aminothiophenol and aldehydes at room temperature.

Method 6

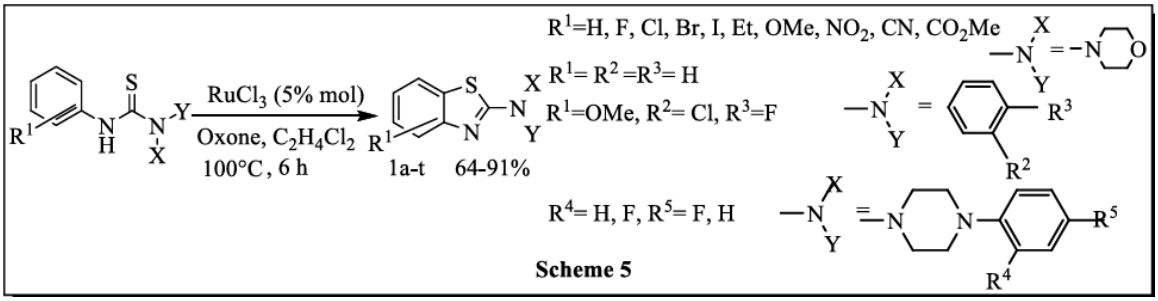
The reaction for the synthesis of benzothiazole proceeds by treating 2-mercaptoaniline with an amine compound in the presence of iodine under ambient conditions (Scheme 4). The use of iodine in the reaction suggests its role as an oxidizing agent or catalyst for the conversion of 2-mercaptoaniline and the amine to benzothiazoles.[6]



Scheme 4

Method 7

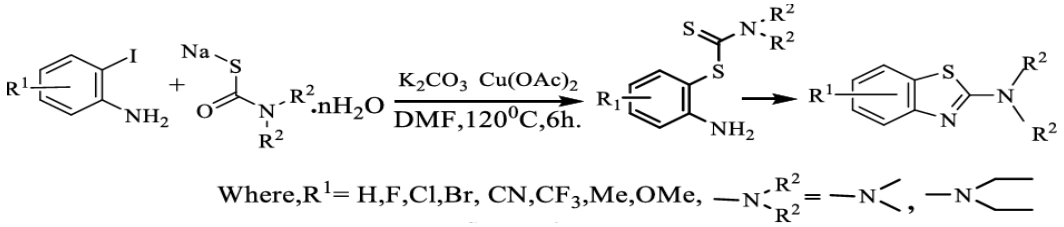
Substituted 2-aminobenzothiazoles were synthesized through from N-arylthiourea in a one-pot reaction using $RuCl_3$ as the transition metal catalyst (Scheme 5). The reaction proceeded by the deprotonation of N arylthiourea with base to form an intermediate which then reacted with 2-bromoaniline to form a new intermediate. In the next step, $RuCl_3$ acted as a catalyst to facilitate the intramolecular cyclization of the intermediate leading to the formation of the final product, substituted 2-amino benzothiazoles, in up to 91% yield. The reaction was found to be more efficient with electron rich substrates as compared to electron deficient ones.[6]



Scheme 5

Method 8

The synthesis of 2-aminobenzothiazoles from sodium di thiocarbamates and 2-iodoanilines via an Ullmann-like reaction process is a simple and efficient one-pot method (Scheme 6). The reaction is catalysed by copper (II) in the presence of a base and a solvent, and conducted at a temperature of 120^{o}C. In the first step of the reaction, sodium dithiocarbamate is formed by the reaction of CS2 with a primary amine in the presence of a base such as caesium carbonate. Next, 2-iodoaniline is added to the reaction mixture, and the Ullmann-like reaction is catalysed by copper (II) in the presence of solvent such as dimethyl formamide. The reaction proceeds via formation of a copper thiolate intermediate which undergoes C–Ar bond formation with the 2-iodoaniline to form the desired 2-aminobenzothiazole derivative. The yield of the product is high reaching up to 97%, and unaffected by the electronic properties of substituents on the aromatic ring. Therefore, this method provides a useful approach for the synthesis of diverse 2-aminobenzothiazole derivatives.[6]



Scheme 6

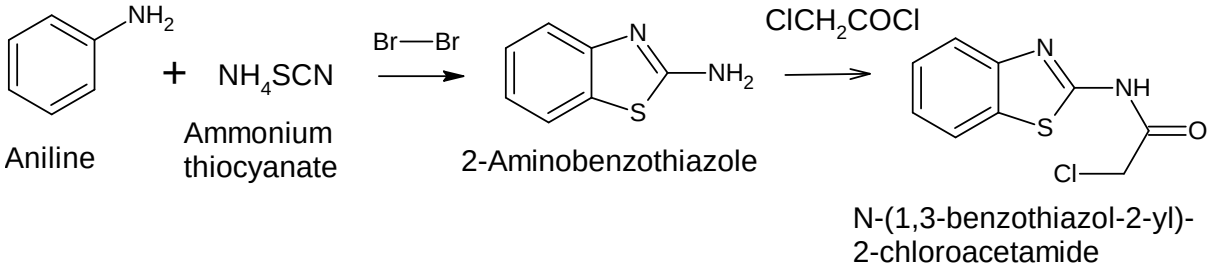
PROCEDURE FOR SYNTHESIS

Preparation of compound 2-aminobenzothiazole

Aniline (4.6 g, 0.05 mol) and ammonium thiocyanate (3.8 g, 0.05 mol) were dissolved in absolute ethanol containing 4 ml of conc. HCl. To this mixture, bromine in glacial acetic acid (6.75 ml, 0.125 mol) was added and the reaction mixture was refluxed for 1 hr. Then it was cooled in an ice bath. The precipitate obtained was filtered, washed with cold water, and dried. The crude product was recrystallized from ethanol.[9] (Scheme 7)

Preparation of compound N-(1,3-benzothiazol-2-yl)-2-chloroacetamide

To a solution of compound (S1) (2.5 g, 0.016 mol) in 30 ml glacial acetic acid, chloroacetyl chloride (3.7 g, 0.032 mol) was added dropwise with constant stirring. The reaction mixture was refluxed for 5 hrs, then it was poured onto crushed ice. The precipitated solid obtained was filtered off, washed with cold water, dried, and recrystallized from aqueous ethanol.[9] (Scheme 7)



Scheme 7

PHARMACOLOGICAL ACTIVITY

The 2-aminobenthiazole scaffold has been extensively explored to construct the structurally diverse analogues with excellent biological activity against various biological targets. Significantly, several therapeutic agents containing this fragment have been approved for clinical application.[1]

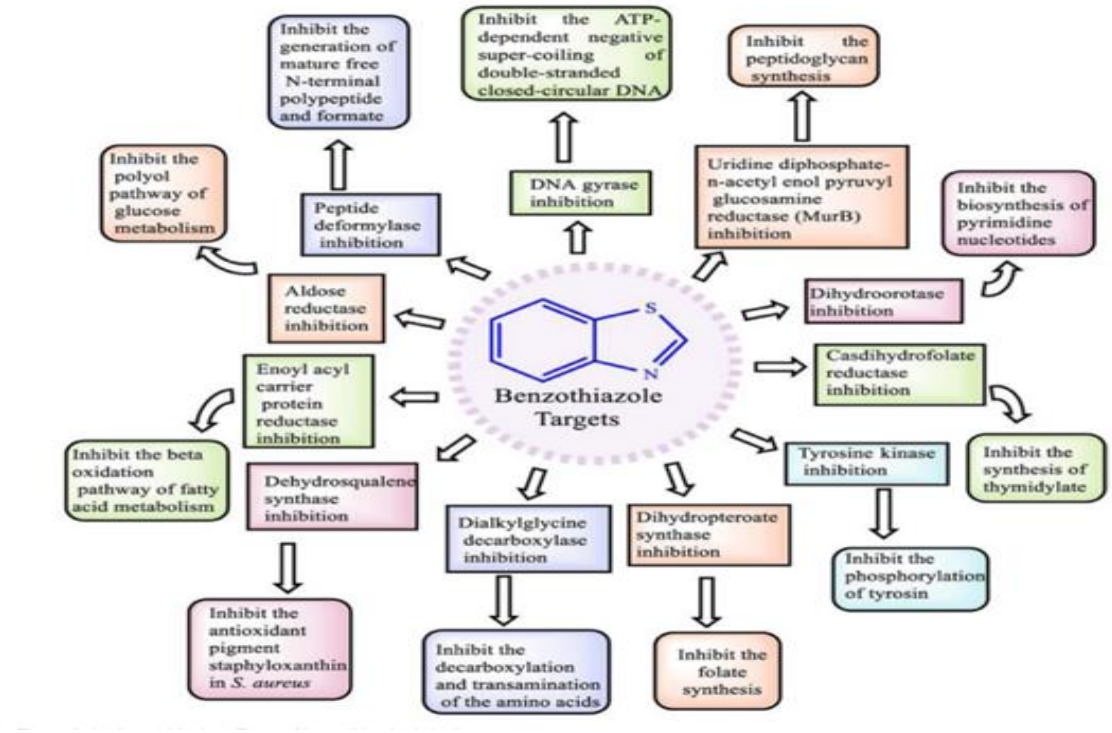


Figure 4: In vitro and in vivo efficacy of benzothiazole derivatives.

ANTICANCER ACTIVITY

1. Ismail *et al.* reported the synthesis of novel pyrimidine-linked 2-aminobenzothiazole derivatives and evaluated their in-vitro anticancer activity against HepG2, HCT116, and MCF-7 human cancer cell lines. Several derivatives exhibited strong cytotoxicity, with some compounds showing superior activity compared to 5-fluorouracil, indicating the potential of 2-aminobenzothiazole scaffolds as promising anticancer agents.[10]

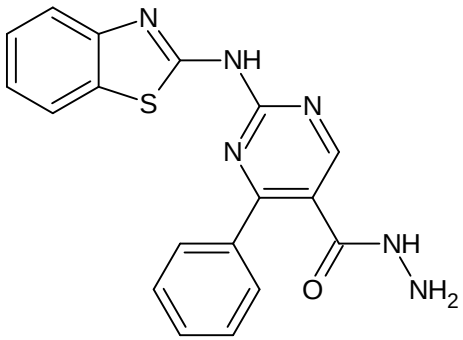


Figure 5: Structure of 2-aminobenzothiazole derivative.

2. Suvarna G Kini and colleagues synthesized 2-aminobenzothiazoles and tested anticancer action. Show N-(6-chloro-1,3-benzothiazol-2-yl)-1-(2,5-dimethoxyphenyl) methanamine has great action.[11]

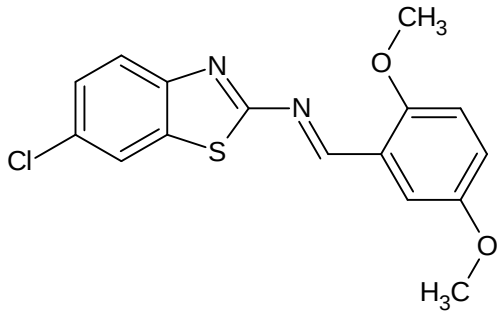


Figure 6: Structure of N-(6-chloro-1,3-benzothiazol-2-yl)-1-(2,5-dimethoxyphenyl) methanamine.

3. Leal K.Z. et al. synthesized of 2-benzthiazole hydrazones derivatives. Anticancer activity was also investigated. The anticancer activity of 2-((2-(benzothiazol-2-yl)hydrazono)benzene-1,4-diol) has been demonstrated.[11]

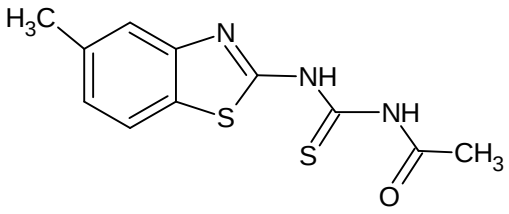
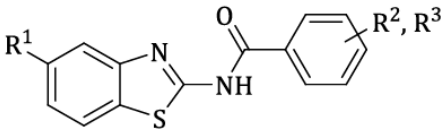


Figure 7: Structure of 2-aminobenzothiazole derivative.

4. Caputo et al. synthesized benzothiazole derivatives with an arylamide or an aryl urea. 60 human tumour cell lines were investigated in a preliminary anticancer assay.[11]



R^1= OMe, OCF_3
R^2 = 4-F, 2-F, 4-OMe
R^3 = H, 6-F

Figure 8: Structure of 2-aminobenzothiazole derivative.

5. Kumbhare et al. synthesized benzothiazolyl thiocarbamides using a catalytic (DMAP) with [bbim][Br3]. The cytotoxic activity of compounds was tested in a mouse melanoma cell line and two human monocytic cell lines (U 937, THP-1).[11]

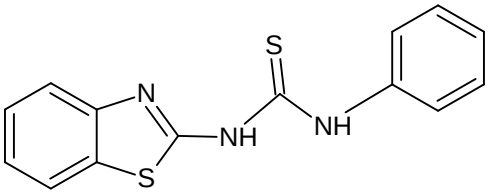


Figure 9: Structure of 2-aminobenzothiazole derivative

ANTIFUNGAL ACTIVITY

1. Liu et al. reported the design and synthesis of benzothiazole (2-aminobenzothiazole) based derivatives as potent inhibitors of N-myristoyltransferase (NMT). Structural optimization of the 2-ABT scaffold significantly broadened the antifungal spectrum, and the lead compound 6m showed strong in vitro and in vivo activity against *Candida* spp., *Cryptococcus neoformans*, and dermatophytes, with efficacy superior to fluconazole, highlighting 2-ABT derivatives as promising broad-spectrum antifungal agents.[12]

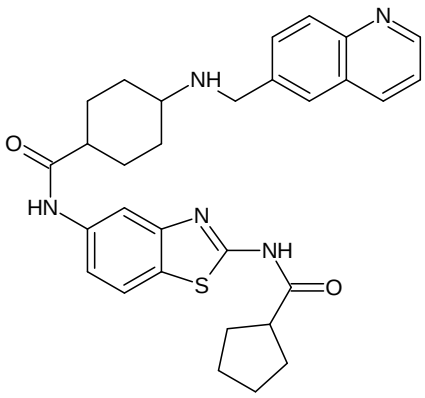


Figure 11: Structure of 2-aminobenzothiazole derivative.

2. Soni and co-workers synthesized 5-[2-(1,3-benzothiazol-2-ylamino)ethyl]-4-(arylideneamino)-3-mercapto-(4H)-1,2,4-triazole, which was investigated for antibacterial and antifungal activity.[11]

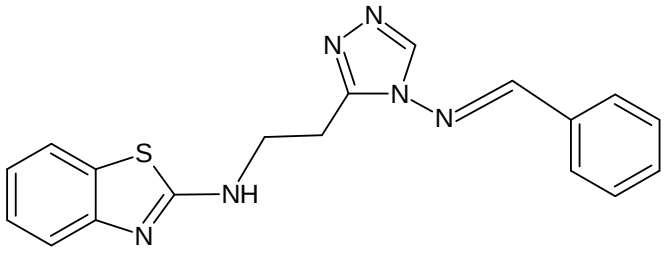


Figure 12: Structure of 2-aminobenzothiazole derivative.

3. Amir M et al. synthesized 1,3,4-thiadiazole and imidazoline derivatives containing benzothiazole and screened for both antibacterial and antifungal activity using cup-plate agar diffusion method. Ofloxacin (50µg/ml) and ketoconazole (50µg/ml) were used as standard drug for antibacterial and antifungal activity respectively. Anti-microbial screening was performed against E. coli, S. aureus, C. albicans and antifungal activity against Aspergillus flavus and Candida albicans.[13]

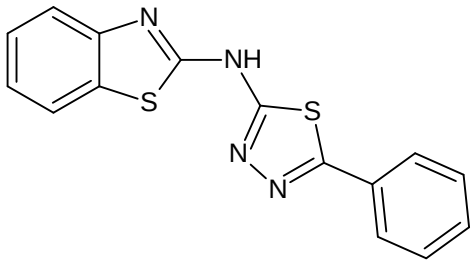


Figure 13: Structure of 2-aminobenzothiazole derivative

ANTI MICROBIAL ACTIVITY

1. Kumbhare RM et al. synthesized new benzothiazole and benzisoxazole from 2-amino 5/6-hydroxybenzothiazole, 6 hydroxy-3-methyl-1, 2-benzisoxal and different dihaloalkanes and screened for their antimicrobial activity against Staphylococcus aureus, and E. coli by disc diffusion method and anti-fungal activity against *Aspergillus flavus*, and *Candida albicans*. Ciprofloxacin (10µg/ml) and fluconazole (10µg/ml) were used as standard drug for antibacterial and antifungal activity respectively.[14]

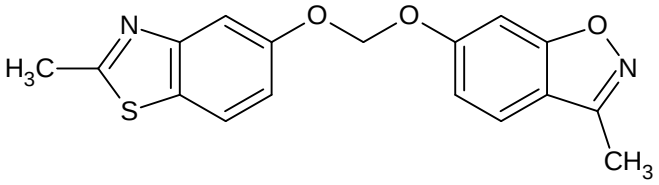


Figure 14: Structure of 2-aminobenzothiazole derivative.

2. Bele et al. synthesized benzothiazole derivatives and S. aureus, S. pyrogens, E. coli, P. mirabilis and A. fumigatus microorganisms were examined for antibacterial efficacy.[11]

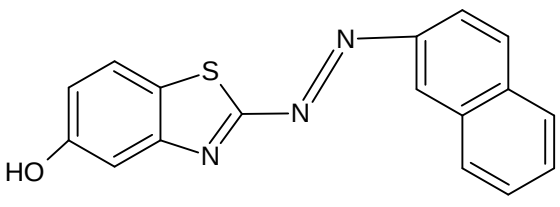


Figure 15: Structure of 2-aminobenzothiazole derivative.

3. Kumar et al. synthesized 2-aminobenzothiazole derivatives, and Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa, and Candida albicans microorganisms were examined for antimicrobial efficacy, where several compounds exhibited moderate to significant antibacterial and antifungal activity.[15]

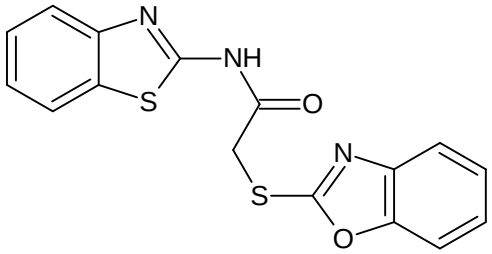


Figure 16: Structure of 2-aminobenzothiazole derivative.

ANTIDIABETIC ACTIVITY

1. Mariappan G et al. synthesized a benzothiazole derivative and showed that N-(6-chlorobenzo[d]thiazol-2-yl)-2-morpholinoacetamide has antidiabetic action.[11]

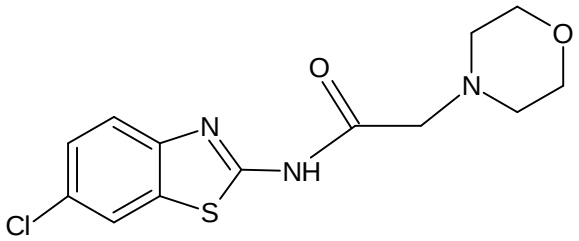


Figure 17: Structure of 2-aminobenzothiazole derivative.

2. Meltzer-Mats et al. reported the synthesis of benzothiazole (2-ABT–based) derivatives as activators of AMP-activated protein kinase (AMPK). These compounds enhanced AMPK-dependent glucose uptake and GLUT4 translocation in L6 myotubes, and a lead derivative significantly reduced blood glucose levels in hyperglycaemic KKAy mice, highlighting benzothiazoles as promising antidiabetic agents.[16]

ANTHELMINTIC ACTIVITY

1. Munirajasekhar et al. reported the synthesis of 2-aminobenzothiazole (2-ABT) derivatives substituted at the 5 and 6 positions and evaluated them for anthelmintic activity against *Eudrilus eugeniae* and *Megascoplex konkanensis*. Most compounds exhibited moderate to significant anthelmintic activity compared with mebendazole, with the 6-nitro-substituted 2-ABT showing the highest potency, highlighting 2-ABT as a promising scaffold for antiparasitic drug development.[17]

2. Sreenivasa M et al. synthesized fluorobenzothiazole comprising sulfonamide pyrazole derivatives. They screened synthesized for anthelmintic activity by using earthworms (*Pheretima posthuma*). Albendazole was used as standard drug. The compounds were evaluated by time taken for complete paralysis and death of worms.[13]

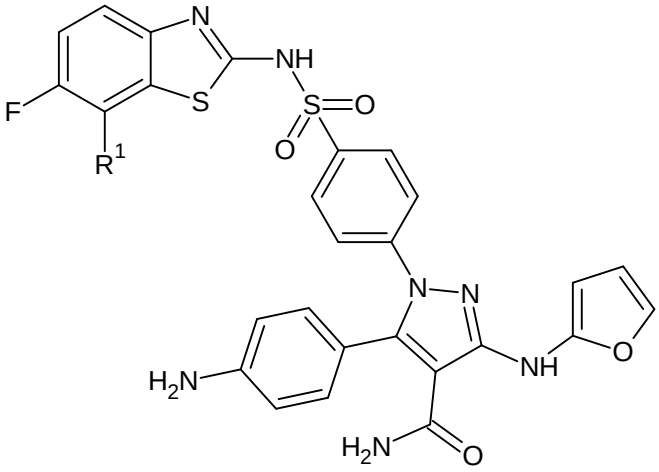


Figure 18: Structure of 2-aminobenzothiazole derivative

SCHISTOSOMICIDAL ACTIVITY

1. Mahran et al. synthesized benzothiazole derivatives and evaluated them for schistosomicidal activity against *Schistosoma mansoni*, with selected compounds showing potent activity comparable to praziquantel.[18]

ANTICONVULSANT ACTIVITY

1. Siddiqui et al. synthesized 6-substituted-2-aminobenzothiazole semicarbazone derivatives, and their anticonvulsant activity was evaluated using the maximal electroshock seizure (MES) model in mice, where several compounds showed 100% protection against seizures without neurotoxicity, indicating potent antiepileptic potential.[19]

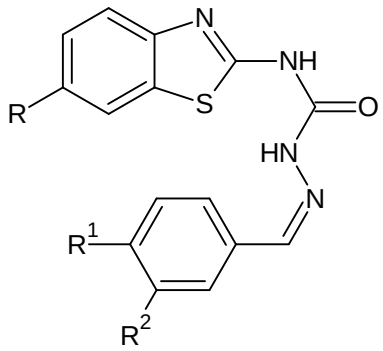
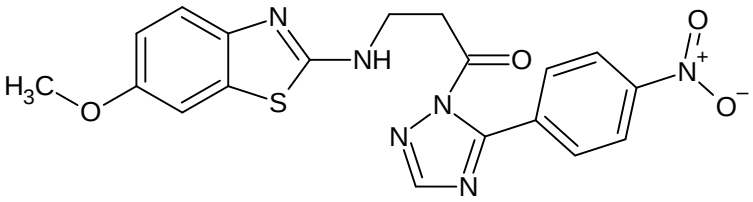


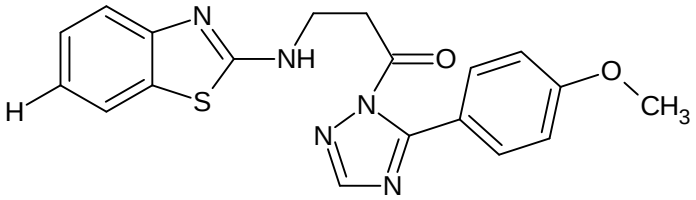
Figure 19: Structure of 2-aminobenzothiazole derivative.

ANALGESIC ACTIVITY

1. Bele and Singhvi synthesized Mannich bases of 6-substituted-2-aminobenzothiazole, and their analgesic activity was evaluated on albino mice using the hot plate method, with acetyl salicylic acid as the reference standard, where several compounds exhibited significant analgesic activity, and derivatives 3d and 3g showed superior analgesic effects compared to the standard drug.[20]



3g



3d

Figure 20: Structure of 2-aminobenzothiazole derivative.

ANTIOXIDANT ACTIVITY

1. Ahmed El-Mekabaty et al. produced a series of benzothiazole derivatives and found antioxidant action and cytotoxicity against the colon cancer cell line (HCT116).[11]

ANTITUBERCULAR ACTIVITY

1. Telvekar et al. synthesized new 2-(2(4arylxybenzyldene) hydrazinyl) benzothiazoles from 2-hydrazinylbenzothiazole and 4-(aryloxy)benzaldehyde using a molecular hybridization technique.[11]

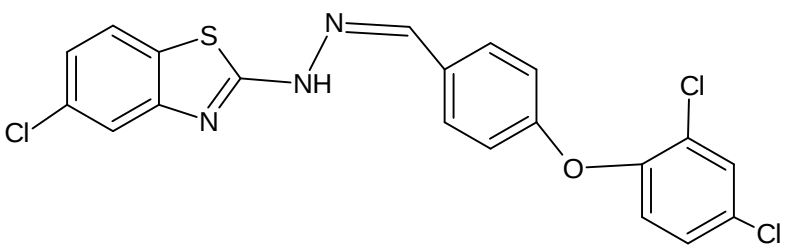


Figure 21: Structure of 2-aminobenzothiazole derivative.

2. Patel et al. evaluated many derivatives of benzmidazolyl-1,3,4-oxadizol-2-ylthio-N-phenyl(benzothiazolyl)acetamides for anti-M. tuberculosis H37Rv activity.[11]

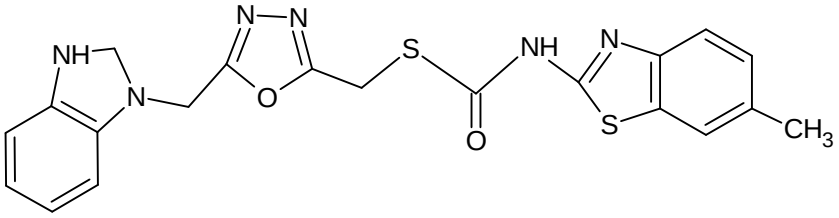


Figure 22: Structure of 2-aminobenzothiazole derivative.

ANTIMALARIAL ACTIVITY

1. Sarkar S et al. synthesized and tested benzothiazole derivatives for antimalarial activity and found that 4-(2-(benzothiazol-2-yl)hydrazonomethyl)benzene-1,2-diol exhibited the highest antimalarial activity.[11]

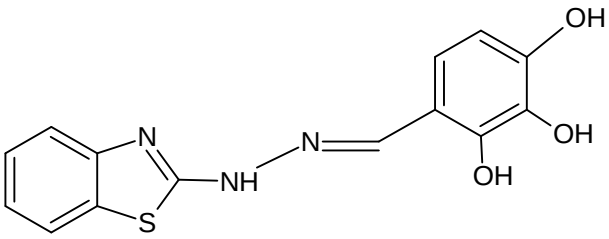


Figure 23: Structure of 2-aminobenzothiazole derivative.

ANTIINFLAMMATORY ACTIVITY

1. Venkatesh and Pandeya synthesized 2-aminobenzothiazole derivatives and evaluated them for anti-inflammatory activity using the carrageenan-induced paw oedema model, with selected compounds showing potency comparable to diclofenac.[21]

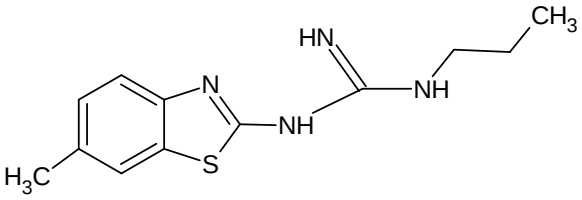


Figure 25: Structure of 2-aminobenzothiazole derivative.

CONCLUSION

This review highlights 2-aminobenzothiazole (2-ABT) as a versatile and privileged heterocyclic scaffold in medicinal chemistry display with a wide range of therapeutic activities. 2-aminobenzothiazole derivatives demonstrate immense potential as antifungal,

anticancer, antidiabetic, anthelmintic, antitubercular, antimalarial, anticonvulsant, anti-inflammatory, analgesic, and antioxidant effects. Among its other effects, anticancer activity is mainly focused as 2-ABT derivatives target several molecular pathways, proteins and enzymes involved in apoptosis.

The SAR studies displayed modification to the nucleus essential for improving biological activity, selectivity, and drug-likeness properties. Improved methods of synthesis have also made it possible to create structurally diverse analogues, which help to refine lead compounds.

Overall, the accumulated evidence confirms that the 2-aminobenzothiazole as a promising structure for future drug development. Rational drug design, biological testing, and in vivo studies could be combined for the creation of effective therapeutic agents, particularly for cancer and infectious diseases.

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