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GLOBAL TRENDS IN THE STUDY OF THE PROPERTIES OF 1,2,4-TRIAZOLE DERIVATIVES (LITERATURE REVIEW)

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ABSTRACT

The relevance of studying 1,2,4-triazole derivatives is driven by their broad application potential in the pharmaceutical, agrochemical, and materials science industries. The discovery of new antifungal agents is crucial due to the increasing prevalence of fungal infections and the emergence of drug-resistant strains. 1,2,4-Triazole derivatives have shown promising antifungal activity, and the presented study aimed to design, synthesise, and evaluate the antifungal potential of a series of new 1,2,4-triazole derivatives. Using an efficient programmed arylation technique, a series of compounds was synthesized and tested for their activity against three human breast cancer cell lines: MDA-MB-231, MCF-7, and ZR-75-1, through *in vitro* growth inhibition assays. At a concentration of 10 µM, the compounds exhibited anticancer activity in the MCF-7 cell line, with one molecule showing the highest efficacy (IC50 = 4.8 µM). Mechanistic studies indicated an increase in pro-apoptotic protein levels in malignant cells along with permeabilization of the outer mitochondrial membrane, hallmark signs of apoptosis. Further investigations into metabolic stability in various liver microsomes revealed favorable pharmacokinetic properties for the compound. For the first time, we have systematically and comprehensively analyzed and summarized global trends and advancements over the past two years in the study of the properties of 1,2,4-triazole derivatives. The necessity and feasibility of further scientific research in this chosen area have been substantiated.

KEYWORDS: 1,2,4-triazole derivatives, physicochemical properties, biological properties, *in silico*, *in vitro*, *in vivo* studies, computer-based predictive models.

INTRODUCTION

The relevance of studying 1,2,4-triazole derivatives is driven by their broad application potential in the pharmaceutical, agrochemical, and materials science industries. These heterocyclic compounds, due to their chemical structure, exhibit diverse biological activities, making them promising candidates for the development of new drugs. 1,2,4-triazole derivatives often demonstrate antimicrobial, antitumor, antiviral, antifungal, and anti-inflammatory properties. Moreover, some of them are used in the creation of new materials, such as polymers and liquid crystals. The importance of their research is further heightened in the context of environmental safety, as they are less toxic compared to some other chemical agents.

1,2,4-Triazole derivatives exhibit a wide range of biological activities and are actively utilized in the development of fungicides and herbicides, which are crucial for plant protection in agriculture. This contributes to high crop yields and enhanced resistance to diseases. Some of these derivatives are also of interest in materials science, as they can be applied in the production of novel materials with unique properties, such as catalysts or materials with high corrosion resistance. Triazole compounds show potential in nanotechnology, where the creation of stable and functional surfaces is essential. Additionally, 1,2,4-triazole derivatives can act as potential enzyme inhibitors that regulate metabolic processes, opening new possibilities for the development of innovative pharmaceuticals. Thus, research on 1,2,4-triazole derivatives holds broad prospects for advancing medicine, agriculture, and cutting-edge technologies.

Hence, the **aim** of our work was to analyze and summarize global achievements in recent years regarding the study of the properties of 1,2,4-triazole derivatives and to substantiate the necessity and feasibility of further research in this scientific direction.

MATERIALS AND METHODS

Heterocyclic compounds are considered one of the primary and most widespread groups of organic compounds. Today, the demand for these compounds is growing daily due to their immense synthetic and biological significance and applications. For instance, these substances exhibit unique antibacterial effects against various Gram-positive and Gram-negative bacterial strains, as well as fungi. Some of them show excellent antibacterial activity, while others demonstrate moderate effectiveness.

The global need for innovative drugs to treat life-threatening diseases is increasing. Due to the widespread availability of antibiotics, bacterial resistance to them is rising, highlighting the urgency of developing new, original medications. Additionally, other fields deserve attention, where modern progressive scientific advancements related to 1,2,4-triazole derivatives provide significant impetus for further development.

RESULTS AND DISCUSSION

Original research on the antagonistic activity of new fluorine-containing 1,2,4-triazole-3-thiones against various strains of opportunistic microorganisms, including *Klebsiella pneumoniae*, *Serratia ficaria*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, and the microscopic fungi *Candida albicans*, has been conducted as part of national studies[1] The authors quantitatively analysed and assessed the purity of the cultures using bacterioscopy and microscopy. According to the researchers, the study results demonstrate that 4-phenyl-5-trifluoroethyl-1,2,4-triazole-3-thione and 4-phenyl-5-pentafluoroethyl-1,2,4-triazole-3-thione exhibited the highest efficiency in inhibiting the growth of *Staphylococcus aureus* and S*erratia ficaria,* respectively. These compounds have shown promise as antimicrobial

agents, indicating their potential application in various treatment and infection prevention scenarios. The obtained results provide a foundation for improving these molecules, functionalizing them, and identifying optimal promising structures.

Another study focuses on determining the enthalpy of formation for several amino-1,2,4-triazole derivatives.[2] Experimentally, the enthalpies of formation of the crystalline phase were obtained using calorimetry, while the enthalpies of sublimation were determined using Calvet microcalorimetry.

Triazoles are an important class of compounds with broad potential applications. Significant interest lies in the functionalization of the triazole itself. In[3], the authors revealed an unusual latent reactivity of the 1,2,4-triazole core, involving N-N bond cleavage and ring opening. This novel reactivity was induced by Sato-Miura-type C-H activation-annulation in the 1,2,4-triazole cycle. This unique reaction enabled facile access to a new class of asymmetrically substituted 2,2'-dipyridylamines with one pyridine ring fully substituted by alkyl groups. These asymmetric 2,2'-dipyridylamines were utilized in the development of targeted drop-selective visualization probes for biomedical applications.

Hydrogen and halogen bonding are important non-covalent interactions that play a significant role in the crystalline structure of organic molecules. An original approach for an in-depth analysis of the crystal packing of two previously synthesized crystalline structures of dihalogenated 1,2,4-triazole derivatives, namely 3,5-dichloro-1H-1,2,4-triazole and 3,5-dibromo-1H-1,2,4-triazole, is proposed by the team of authors.[4] This study provides insights into the complex interplay of hydrogen and halogen bonding, which leads to the formation of several trimeric structures in the crystalline molecules of 1,2,4-triazole derivatives.

Platinum(II) and Platinum(IV) Chemistry with 3,4,5-Tris(2-pyridyl)-4-H-1,2,4-triazole and 3,5-Di(2-pyridyl)-4-(4-pyridyl)-4-H-1,2,4-triazole Ligands is described in work.[5] Electron-rich dimethylplatinum (II) complexes undergo oxidative addition reactions with methyl iodide or dichloromethane, forming various complexes, each appearing as a mixture of three isomers.

The objective of another study was to evaluate the antimicrobial, antitumor, and antioxidant activities of 1,2,4-triazole derivatives.[6] The findings demonstrate the positive role of these compounds as antimicrobial, antifungal, and antiradical agents, particularly against *Candida albicans*, significantly reducing fungal growth. Furthermore, the compounds exhibited no cytotoxicity while actively targeting cancer cells.

A series of pyrazolyl[1,2,4]triazoles was synthesized by reacting multifunctionalized triazoles with symmetric and asymmetric β-dicarbonyl compounds in orthophosphoric acid.[7] Additionally, a novel series of molecules, including 6-methyl-6-aryl-5,6-dihydro[1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine-3-thiol and 9-amino-5-methyl-3,5-diphenyl-8-sulfanyl-2,4,5,9-tetrahydro-3H-[1,2,4]triazolo[5,1-c][1,2,4]triazepin-3-ol, was successfully synthesized through the reaction of triazoles with acetophenone derivatives.

A series of new pyridine-1,2,4-triazoles was obtained by researchers.[8] These compounds were synthesized from 1,2,4-triazole-3-thiopropagyl derivatives and various azides. The cytotoxic activity of the compounds was assessed through screening against three cancer cell lines, including human colon carcinoma (HCT116), human cervical carcinoma (HeLa), and human breast adenocarcinoma (MCF7). Additionally, antimicrobial evaluation was performed against one

Gram-positive bacterium (*Staphylococcus aureus ATCC 29,213*), two Gram-negative bacteria (*Sarcina lutea* and *Escherichia coli ATCC 25,922*), and one fungal strain (*Candida albicans NRRL Y–477*). The molecular docking study of the synthesized compounds was used to evaluate their ability to bind to the target enzyme. Based on the results of *in vitro* and *in silico* studies, these compounds may be useful in the development of potential antimicrobial drug candidates.

A series of 4-halogenoaryl-5-(thiophen-2-yl or 5-bromothiophen-2-yl)-2,4-dihydro-3H-1,2,4-triazol-3-thiones was synthesized by reacting thiophene-2-carbohydrazide or 5-bromothiophene-2-carbohydrazide with various halogenaryl isothiocyanates followed by cyclisations through heating in an aqueous sodium hydroxide solution.[9] The compounds exhibited significant activity against both Gram-positive and Gram-negative bacteria. Moreover, some of them showed potent antiproliferative activity against HepG-2 and MCF-7 cancer cell lines (IC50 < 25 μM). Noteworthy is the literature review aimed at summarizing the antitubercular profile of 1,2,4-triazoles, one of the most sought-after scaffolds with a broad spectrum of biological and pharmacological activities.[10] The authors argue that the pharmacophore "triazole" has replaced the widely used "imidazole" as a "systemically integral azole," combining synchronicity with randomness. The extensive body of research conducted over the past two decades on the 1,2,4-triazole fragment provides an inevitable foundation for the development of novel potential drugs with improved efficacy, selectivity, and reduced toxicity.

Pain and inflammation are major debilitating problems typically treated with NSAIDs (non-steroidal anti-inflammatory drugs). The presented study focuses on investigating the analgesic and anti-inflammatory properties of 1,2,4-triazole derivatives.[11] The anti-inflammatory properties of 1,2,4-triazoles were evaluated using formalin-induced paw edema and acetic acid-induced writhing tests, while their peripheral and central analgesic effects were assessed through the hot plate method. The evaluation demonstrated that (5-(4-nitrophenyl)-1-phenyl-1H-1,2,4-triazol-3-(2H)-one reduced the number of writhes in animals, increased reaction time in the hot plate method, reduced swelling, and decreased exudate volume.

Triazole scaffolds play a significant role in a wide range of biological functions. Many compounds containing the triazole fragment exhibit important antimicrobial, anticancer properties, and more. Additionally, the triazole scaffold demonstrates remarkable antiviral activity in both nucleoside and non-nucleoside analogs. Numerous synthetic methods have been developed by scientists worldwide as a result of their broad spectrum of biological capabilities.

In the presented review, the authors attempt to summarize the novel synthetic methods developed by various research groups and provide a comprehensive description of the role of [1,2,4]- and [1,2,3]-triazole derivatives as antiviral agents.[12] It has been shown that antiviral triazole compounds affect a wide range of molecular proteins. Furthermore, several strains of viruses, including human immunodeficiency virus, SARS virus, hepatitis B and C viruses, influenza virus, and herpes virus, have been found to be sensitive to triazole derivatives.

Condensed heterocycles based on 1,2,4-triazole exhibit a broad spectrum of biological activities. Introducing a pharmacophore fragment of a tertiary aryl residue significantly enhances the bioactivity of the resulting compounds. Therefore, the synthesis of condensed derivatives of symmetrical 1,2,4-triazole with aryl tellurium fragments is a relevant task.[13] One of the most convenient and efficient methods for introducing an aryl tellurium fragment into such systems is the method of electrophilic intramolecular cyclisation of alkenyl derivatives of azole heterocycles.

This study is aimed to determine the effect of the substituent's nature in the fifth position of the initial N-allyl derivatives of 1,2,4-triazol-3-thione on the regioselectivity of electrophilic heterocyclisation with p-methoxyphenyltellurium trichloride. The discovery of new antifungal agents is crucial due to the increasing prevalence of fungal infections and the emergence of drug-resistant strains.

1,2,4-Triazole derivatives have shown promising antifungal activity, and the presented study aimed to design, synthesise, and evaluate the antifungal potential of a series of new 1,2,4-triazole derivatives.[14] The compounds were characterized using FTIR, NMR, and MS methods. To assess the potential of the synthesized compounds as antifungal agents, *in silico* studies were conducted, including ADME properties, drug-likeness, and molecular docking. *In vitro* antifungal activity against *Candida albicans* and *Aspergillus niger* was evaluated using the agar well diffusion method, and inhibition zones were measured. All synthesized compounds demonstrated promising antifungal activity.

In another study, the authors synthesized and characterized a ring system with new 1,2,4-triazole compounds.[15] The anticancer properties of these compounds were investigated by assessing their activity against breast cancer (MCF-7) and colorectal cancer (HCT-116) cell lines. The MTT assay results for MCF-7 cells showed that some substances demonstrated significant cytotoxic activity, with IC50 values of 38 µM and 53 µM.

Ribavirin and its analogs exhibit *in vitro* antiproliferative activity against cancer cells. In this study, researchers explored the biological activity of a series of alkyl/aryloxymethyl derivatives of ribavirin's aglycone, 1,2,4-triazole-3-carboxamide.[16] The authors assessed their antiproliferative and antimicrobial effects. The results revealed that certain derivatives induce leukemia cell death at low micromolar concentrations and inhibit cell cycle progression. Molecular docking findings suggest that these compounds may act by inhibiting translation initiation, making them potential candidates for cancer treatment.

Through intramolecular cyclization, the authors synthesized bis-(1,2,4-triazoles).[17] The chemical structures of the synthesized compounds were confirmed using 1H NMR and 13C NMR spectroscopy. Additionally, the ability of the synthesized compounds to inhibit urease enzyme was evaluated *in vitro* using the Weatherburn method. All compounds showed urease inhibition within the range of 15.00 ± 0.10 to 16.00 ± 0.25 IC50 (µg/mL), comparable to the standard thiourea (IC50 = 15.75 ± 0.15 µg/mL).

Perfluorosulfonic acid (PFSA) polymers are widely used as electrolyte membranes in polymer electrolyte fuel cells. To investigate the impact on proton conductivity through control of structural orientation, the researchers incorporated 1,2,4-triazole into PFSA films during casting to introduce anisotropy into the ion-cluster structure of the films.[18] It was found that proton conductivity was high along the film surface direction and low along the thickness direction. Structural analysis using small-angle X-ray scattering suggested that this anisotropy in proton conductivity was due to anisotropy in the ion-cluster structure, attributed to the formation of a phase-separated structure caused by the strong interaction between sulfonic acid groups and 1,2,4-triazole during film casting and surface fluorine segregation.

Another study reported compounds containing two 1,2,4-triazole cores.[19] These molecules demonstrated significant broad-spectrum antimicrobial and anticancer activities. The authors highlighted directions for future research focusing on evaluating their efficacy in biological models, understanding their mechanisms of action, and developing more potent bis-triazole derivatives as potential effective drugs.

Researchers propose original methods for synthesizing a series of 4-azo derivatives of 1,2,4-triazole through the reaction of molten thiocarbohydrazide with various substituted benzoic acids.[20] These compounds were subsequently coupled with different aromatic amines to obtain 4-azo derivatives of 1,2,4-triazole. The synthesized derivatives were then converted into polymers of 4-azo-3,5-substituted 1,2,4-triazole using dry acetonitrile, pyridine, and polyacryloyl chloride. The resulting substances demonstrated potent antibacterial and anticorrosion properties.

Hydrazine and its derivatives have traditionally served as fuel for several decades. However, their extreme toxicity, carcinogenicity, high volatility, and environmental impact have necessitated reconsidering their direct use. To synthesize environmentally friendly dual fuels with high density, specific impulse, and thermal stability, three novel N-alkyl-1,2,4-triazole-borane complexes were successfully prepared by reacting alkylated 1,2,4-triazole coordinated with sodium borohydride in the presence of ammonium sulfate.[21] The results indicate their significant potential as hypergolic fuels or hypergolic ionic liquid additives in hypergolic materials applications.

In recent years, scientists have extensively studied synthetic platforms and reactions of 1H- and 4H-1,2,4-triazole derivatives with various biologically active substituents on nitrogen and/or carbon atoms.[22] The presented study explores synthetic approaches for obtaining mono-, di-, tri-, and tetra-substituted 1,2,4-triazole structures.

Thiazoles and pyrazolo[5,1-c][1,2,4]triazoles have garnered significant attention due to their biological and therapeutic effects. Consequently, researchers have proposed innovative studies to develop new heterocyclic compounds featuring thiazole and pyrazole.[23] The authors achieved this by combining 2-cyano-N-(5-methylthiazol-2-yl)acetamide with cinnamaldehyde to synthesize two distinct chemical compounds.

The antioxidant activity of some of the obtained compounds was evaluated using DPPH free radical scavenging assays conducted in triplicate. Average values were considered, with ascorbic acid used as a reference standard, and all tested compounds demonstrated antioxidant activity.

Another research team reported the synthesis, anticancer activity, and metabolic stability of diarylated 1,2,4-triazole molecules.[24]

Using an efficient programmed arylation technique, a series of compounds was synthesized and tested for their activity against three human breast cancer cell lines: MDA-MB-231, MCF-7, and ZR-75-1, through *in vitro* growth inhibition assays. At a concentration of 10 μM, the compounds exhibited anticancer activity in the MCF-7 cell line, with one molecule showing the highest efficacy (IC50 = 4.8 μM).

Mechanistic studies indicated an increase in pro-apoptotic protein levels in malignant cells along with permeabilization of the outer mitochondrial membrane, hallmark signs of apoptosis. Further investigations into metabolic stability in various liver microsomes revealed favorable pharmacokinetic properties for the compound.

CONCLUSION

For the first time, we have systematically and comprehensively analyzed and summarized global trends and advancements over the past two years in the study of the properties of 1,2,4-triazole derivatives. The necessity and feasibility of further scientific research in this chosen area have been substantiated.

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