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OXYGEN & NITROGEN CONTAINING HETEROCYCLIC COMPOUNDS: A BOON FOR ANTINEOPLASTIC RESEARCHES

Mandeep Singh Chhina¹, Puja Gulati^{* 1}, Prabhsimran Singh², Sukhmanpreet Singh¹ and Aanchal Khanna³

School of Pharmacy¹, Desh Bhagat University, Mandi Gobindgarh - 147301, Punjab, India.

Khalsa College of Pharmacy², Amritsar - 143001, Punjab, India.

Department of Pharmaceutical Sciences³, Guru Nanak Dev University, Amritsar - 143005, Punjab, India.

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Correspondence to Author:

Dr. Puja Gulati

Professor,
School of Pharmacy,
Desh Bhagat University, Mandi
Gobindgarh - 147301, Punjab, India.

E-mail: Puja_duggal@yahoo.co.in

ABSTRACT: Heterocyclic compounds have emerged as a focal point in medicinal and biological research due to their diverse applications. Their unique structures, often incorporating atoms like nitrogen, oxygen, or sulphur within their rings, offer a wide range of potential therapeutic properties. These compounds form the backbone of over 90% of novel drugs, bridging the gap between chemistry and biology. Their versatility extends to pharmaceuticals, agrochemicals, and veterinary products. Heterocyclic compounds exhibit a broad spectrum of biological activities, including antifungal, anti-inflammatory, antibacterial, antiviral, antioxidant, anticonvulsant, anthelmintic, antipyretic, anti-allergic, anti-histamine, herbicidal, anticancer, antihypertensive, and anti-leprosy effects. Beyond the existing market, numerous heterocyclic compounds are currently under investigation for their promising potential against various malignancies. Oxygen based heterocycles (Oxazole) serve as the foundational structures of numerous biologically active compounds and FDA-approved drugs. While nitrogen-based heterocycles have been extensively explored as potential anticancer agents, there is growing interest in oxygen and nitrogen-based heterocycles as a promising avenue for innovative drug discovery. Fusing multiple heterocyclic rings together is a common strategy to enhance the biological properties of molecules. Despite advancements in anticancer therapies like 5-fluorouracil, doxorubicin, methotrexate, and daunorubicin, cancer remains a significant health challenge. Apart from these various nitrogen containing compounds and derivatives like quinolines have also marked their presence in the anticancer treatments. Novel fused heterocycle derivatives have been synthesized or are under progress. To address this, researchers are actively exploring the synthesis of novel fused and spiro heterocyclic compounds, aiming to identify potent anticancer agents with improved efficacy and reduced side effects.

INTRODUCTION: Cardiovascular disorders are the major cause of mortality globally, with cancer coming in second¹. Among the most common and fatal cancers are hepatocellular carcinoma (HCC) and colorectal cancer (CRC)^{2, 3}. HCC, a liver cancer, carries a high mortality rate^{2, 4}.

Several factors contribute to HCC development, including chronic viral hepatitis infections, exposure to aflatoxin, obesity, and excessive alcohol consumption^{5, 6}.

Currently, the sole FDA-approved treatment for HCC is Sorafenib, a medication that can only modestly extend patient survival⁷. While HCC rarely spreads beyond the liver, there is growing evidence for rare cases of colon metastasis, which are currently treated solely with surgical resection⁸. The second most common cause of mortality from cancer is colorectal cancer (CRC), which is

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also extremely deadly⁹. Standard cancer therapies, including radiation, chemotherapy, and surgery, are often combined with immunosuppressive drugs to manage the patient's immune response, leaving them more susceptible to infections¹⁰. Unfortunately, none of these treatments are perfectly selective for cancer cells, and they often cause severe side effects. As a result, there is a critical need for new, highly selective anticancer agents with potent antimicrobial properties to improve patient outcomes¹¹.

Heterocyclic Drugs in Cancer Treatment: Over the past few decades, many anticancer drugs have been derived from synthetic compounds^{11, 12}. Heterocyclic molecules, which contain two or more different elements in their ring structure, have received considerable attention in the development of pharmacologically active agents and advanced materials^{13, 14}. In fact, heterocyclic compounds account for over 75% of clinically used drugs today¹⁵. Due to their diverse biological and pharmacological applications, sulphur, nitrogen, and/or oxygen-containing heterocycles like thiophene and pyrazole are particularly interesting to medicinal chemists^{16, 17, 18}.

Fused Heterocycles: Fused heterocycles, where multiple heterocyclic rings are linked together, have emerged as a promising class of candidates for anticancer drug discovery. One particularly intriguing combination for anticancer applications is the fusion of furan, oxazole, and quinoline rings.

Furan: This five-membered ring containing oxygen, known as a furan, has demonstrated antitumor properties. Research suggests that furans can disrupt various cellular processes essential for

cancer cell growth and survival, such as cell cycle progression and the formation of new blood vessels (angiogenesis). A furan unit is included in a number of commercially marketed medications, such as the anti-microbial medications diloxanide, cefuroxime, and ceftiofur as well as the non-steroidal anti-inflammatory pharmaceuticals refecoxib and firocoxib¹⁹.

Peptide-Conjugated Heterocycles for Cancer Treatment: Compounds combining peptides (short chains of amino acids) with heterocycles (compounds with ring structures containing other elements besides carbon) are a valuable class of medications²⁰. In a recent research, a library of short peptide sequences based on a 2-amino-3-(3',4',5'-trimethoxybenzoyl) benzo[b]furan scaffold was discovered to have remarkable therapeutic potential against cancer cell types, including HeLa cells²¹. Additionally, research has shown that tripeptides (peptides with three amino acids) linked to a furan moiety at their C-terminus (end) can inhibit protease enzymes with greater selectivity and increased effectiveness, while also exhibiting antineoplastic (anti-cancer) activity²². It has been observed that the West Nile virus (WNV) and dengue virus (DENV) proteases are inhibited by furan-capped tripeptides that include uncommon amino acids²³. Several studies have shown that peptides containing D-amino acids (mirror images of natural L-amino acids) or nonnatural amino acids with modified side chains (peptidomimetics), along with cyclization (joining the ends to form a ring) to block the N- and C-termini, can have increased rigidity, making them less susceptible to degradation by proteases²⁴⁻²⁶.

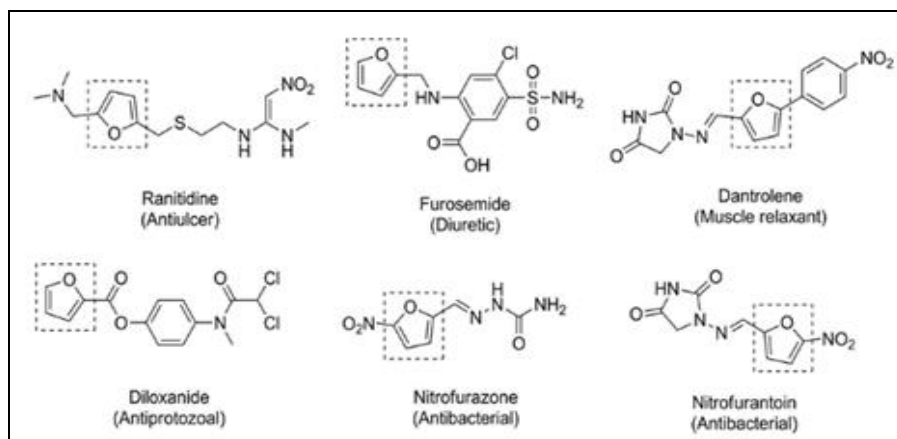


FIG. 1: PHARMACOLOGICALLY ACTIVE FURAN DERIVATES AND USES

Building on this prior research, the current study aimed to synthesize and evaluate the anticancer properties of a furan moiety conjugated with a tripeptide sequence incorporating a combination of natural, unnatural, hydrophobic (water-fearing), and cationic (positively charged) amino acid residues. The goal was to develop novel conjugates with improved resistance to protease breakdown and assess their potential effectiveness against human cervical cancer cells.

Oxazole's Potential in Cancer Treatment:

Oxazole, another five-membered ring containing nitrogen and oxygen, has emerged as a promising scaffold in cancer research. Studies have shown that certain oxazole derivatives can inhibit enzymes crucial for tumor cell growth and spread (metastasis)^{27, 28}. This five-membered ring structure, frequently found in both natural products and synthetic molecules, is recognized as a valuable starting point for drug discovery.

The structural and chemical diversity offered by the oxazole ring allows for various interactions with receptors and enzymes, leading to a wide range of biological activities. This versatility positions oxazole-based molecules as a cornerstone in medicinal chemistry, contributing significantly to the development of novel therapeutic agents²⁹⁻³¹. Consequently, a vast array of oxazole-containing compounds, both approved drugs and potential candidates, are actively explored for the treatment of diverse diseases, including bacterial infections⁶⁻⁸, fungal infections³²⁻³⁴, inflammation³⁵⁻³⁷, viral infections³⁸⁻⁴⁰, tuberculosis⁴¹⁻⁴³, cancer⁴⁴⁻⁴⁶, parasitic infections⁴⁷⁻⁴⁹, diabetes⁵⁰⁻⁵⁵, and many more. This revised version eliminates direct quotes and rephrases sentences while maintaining the key points about oxazole's potential in cancer treatment, its structural advantages, and its diverse applications in medicine. The references are retained for clarity.

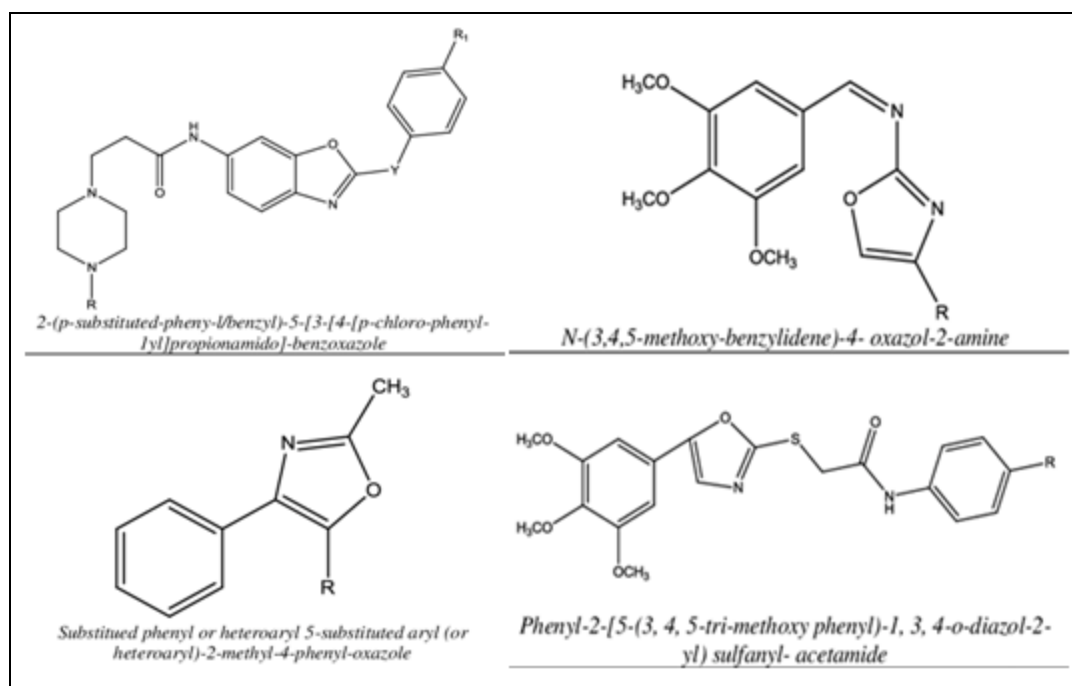


FIG. 2: PHARMACOLOGICALLY ACTIVE OXAZOLE DERIVATIVES

Quinolines in Cancer Treatment: The two-ringed aromatic system called quinoline forms the backbone of many established anticancer drugs. These quinoline-based drugs can target various processes within cancer cells, including DNA replication and the activity of topoisomerases (enzymes that manage DNA structure). Quinoline, formula C₉H₇N, is a heterocyclic aromatic compound. Other names for quinoline include

benzopyridine, benzo[b]pyridine, 1-benzazine, and benzazine. This hygroscopic liquid is yellowish and oily, with slight solubility in water but good solubility in alcohol, ether, and various organic solvents. Isoquinoline, a close relative of quinoline, differs by the position of its nitrogen atom (at the second position)⁵⁶. Versatile Building Block for Medicinal Chemistry: Quinoline derivatives serve as valuable starting points (or "parental

compounds") for synthesizing molecules with therapeutic applications, particularly those with antimalarial and antimicrobial properties. Many quinolines and their derivatives exhibit a range of biological activities, including antimicrobial, antitumor, antifungal, hypotensive, anti-HIV, analgesic, and anti-inflammatory effects. Recent research has explored how quinoline and its

analogues function in inhibiting tyrosine kinases, proteasomes, tubulin polymerization, topoisomerases, and DNA repair processes. Studies have shown that strategically substituting groups within a bioactive molecule based on quinoline can significantly influence its pharmacological effects

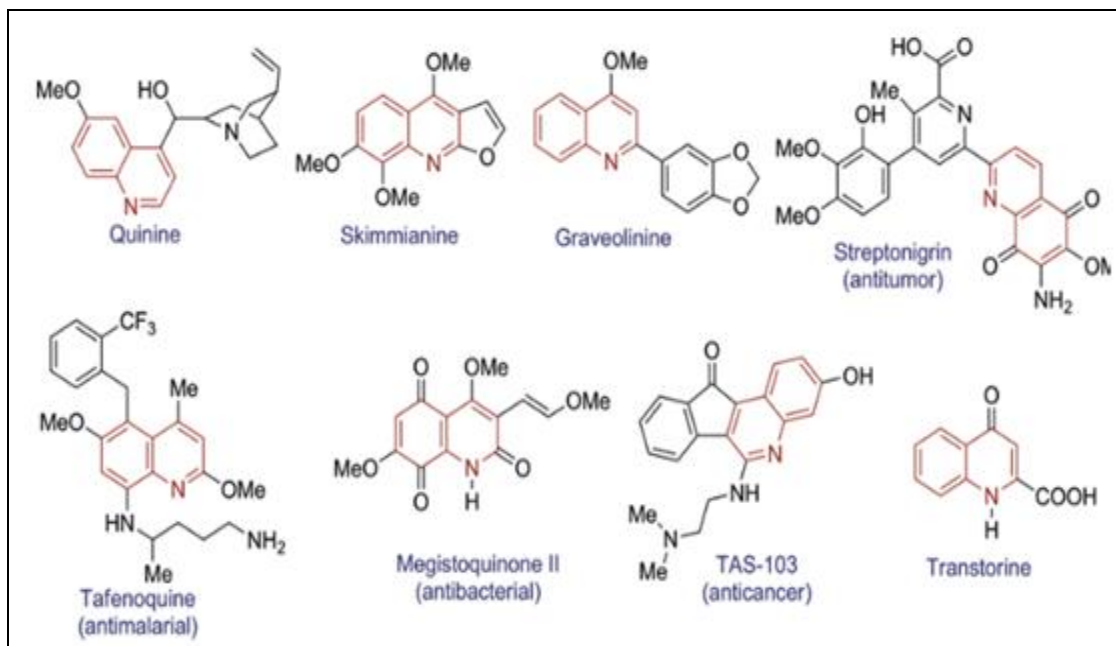


FIG. 3: PHARMACOLOGICALLY ACTIVE QUINOLINES DERIVATIVES AND USES

Previous research has explored various fused heterocyclic derivatives, combining two rings such as furan and oxazole, furan and quinoline, or oxazole and quinoline. These derivatives have

demonstrated a range of pharmacological activities, often exhibiting improved efficacy and reduced side effects compared to existing drugs. Some examples of such derivatives include:

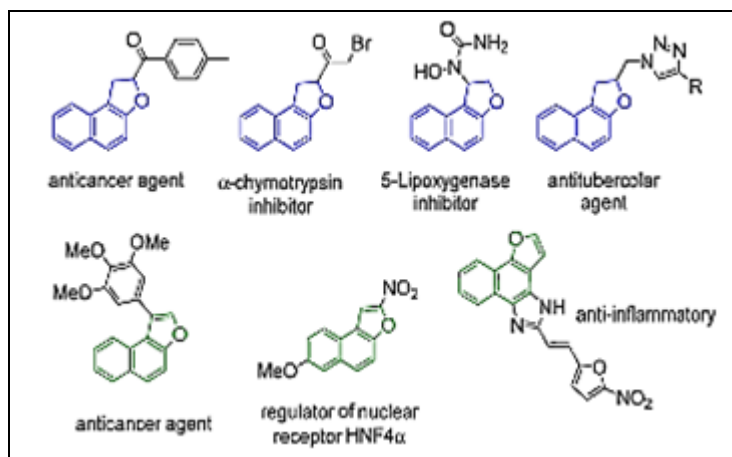


FIG. 4: FUSED HETEROCYCLIC DERIVATIVES AND USES

There is a significant opportunity to discover new molecules by creating fused heterocyclic derivatives that combine hetero molecules like furan, oxazole, and quinolone derivatives.

Research Prospective from Recent Literature: Heterocyclic Compounds as Potent Anticancer Agents: Martins *et al.*, (2015): Heterocyclic compounds have emerged as a cornerstone in

medicinal chemistry due to their prevalence in marketed pharmaceuticals, structural diversity, and unique physicochemical properties. Beyond approved drugs, numerous 7 heterocyclic compounds are under investigation for their potential in cancer treatment, leveraging their adaptable core structures. However, like other promising anticancer agents, these compounds have limitations. This review provides a comprehensive overview of heterocyclic compounds and their medical applications, with a particular focus on cancer therapy. We will examine biochemical mechanisms, biological targets, structure-activity relationships, and challenges associated with these compounds. Furthermore, given the potential of nanotechnology to enhance drug delivery, we will discuss the fundamentals of nanovectorizing heterocyclic compounds to improve their pharmacokinetic and pharmacodynamic profiles⁵⁸.

Chiacchio et al., (2019): Heterocyclic compounds, renowned for their structural and chemical versatility, have emerged as a promising focus for anti-cancer drug discovery. Oxazoles, incorporating oxygen and nitrogen within their core structure, exhibit a propensity for diverse interactions with enzymes and receptors, making them potential candidates for novel therapeutic development. This review delves into recent advancements in the application of oxazole-based compounds to cancer research. It encompasses newly identified iso/oxazole-based drugs, their synthetic methodologies, and the evaluation of their biological activities. Furthermore, the review explores their dehydrogenated counterparts, iso/oxazolines and iso/oxazolidines⁵⁹.

Zheng X, Liu W & Zhang D. (2020): A broad variety of biological actions are displayed by azazole compounds, which have a five-membered ring with one nitrogen and one oxygen atom. Their ability to interact with diverse receptors and enzymes through various non-covalent bonds has made them a focal point for researchers worldwide. The van Leusen reaction, employing tosylmethylisocyanides (TosMICs), has emerged as a prominent method for producing oxazole-based medicinal compounds. This review compiles recent advancements in oxazole synthesis using the van Leusen approach, introduced in 1972. This study aims to identify potential oxazole-based drug

candidates, providing valuable insights for drug discovery and development⁶⁰.

Mohamed MFA & Abuo-Rahma GEA (2020): The strategy of combining multiple therapeutic targets within a single molecule, often referred to as hybridization, has shown promise in drug design. In addition to possibly lowering side effects and drug resistance, this strategy can increase medication efficacy. Merging quinoline and chalcone components has proven to be a fruitful avenue in the search for new anticancer compounds. Many of these hybrid molecules exhibit anticancer properties by interfering with various cellular processes, including tubulin polymerization, kinase activity, and DNA function. Consequently, these compounds can be categorized based on their specific mechanisms of action⁶¹.

Guan YF et al., (2021): Fusing a chalcone moiety with a quinoline scaffold through molecular hybridization could yield promising anticancer candidates. Thus, a number of quinoline-chalcone compounds were developed and synthesised in this investigation, and their anti-proliferative efficacy against the MGC-803, HCT-116, and MCF-7 cell lines was assessed. Compound 12e, with IC50 values of 1.38, 5.34, and 5.21 μ M, respectively, showed remarkable inhibitory effectiveness against all three cell lines among these compounds. Further mechanistic investigations revealed that compound 12e suppressed MGC-803 cell growth in a dose-dependent manner, inhibited colony formation, induced cell cycle arrest at the G2/M phase, and significantly elevated levels of apoptosis-related proteins (Caspase-3/9 and cleaved-PARP).

Additionally, compound 12e markedly increased reactive oxygen species (ROS) production, and its anti-cancer effects on gastric cancer cells were dependent on ROS generation. All things considered, our work suggests that new anti-cancer compounds may be generated by directly attaching a chalcone fragment to a quinoline scaffold, and compound 12e is a promising lead drug for the creation of anticancer therapies. This review focuses on the anticancer potential of quinoline-chalcone hybrids. A comprehensive understanding of these compounds may facilitate the creation of novel, multi-target therapies for cancer treatment⁶².

Bukhari et al., (2022): Novel furan-based compounds were designed, synthesized, and assessed for their ability to inhibit cell growth and tubulin polymerization. Flow cytometry analysis of pyridine carbohydrazide 4 and N-phenyl triazinone 7 revealed disruptions in the G2/M phase of the cell cycle. The accumulation of cells in the preG1 phase, coupled with positive annexin V/PI staining, indicative of genetic material degradation or fragmentation, suggests a potential apoptotic pathway. Moreover, compounds 4 and 7 exhibited potent pro-apoptotic effects by triggering the intrinsic mitochondrial apoptotic pathway. This mechanism was confirmed by an ELISA assay demonstrating elevated p53 and Bax levels, and decreased Bcl-2 expression compared to the control

CONCLUSION: Heterocyclic rings are a fascinating class of organic compounds containing atoms other than carbon in their ring structure. Due to their many pharmacological characteristics, these rings are essential to several biological processes and have generated a great deal of interest in medicinal chemistry. The creation of innovative treatment drugs with increased efficacy and fewer side effects is an ongoing goal in cancer research. Fused heterocyclic rings, where two or more heterocycles are linked together, have emerged as a promising class of candidates for anticancer drug discovery. By combining these three heterocycles into a fused ring system, scientists aim to create molecules that harness the synergistic effects of each individual ring.

This approach can potentially lead to anticancer agents with:

Enhanced Potency: The combined functionalities of the furan, oxazole, and quinoline moieties may result in compounds with greater efficacy against cancer cells.

Improved Selectivity: The specific arrangement of the heterocycles could lead to agents that selectively target cancer cells while minimizing harm to healthy tissues.

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