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Design, Synthesis, And Biological Activity Of Some Novel Quinoline Derivatives

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ABSTRACT

Here, some novel quinoline derivatives are presented in an effort to synthesise some molecules with strong antioxidant activity. First, 7-methyl or 8-methyl substituted 2-cholro-3-formylquinolines (Ia, b) were made utilising the Vilsemeir-Hack reagent method. Additional substitutions of 7-methyl or 8-methyl Compound (I) reacted with 4M HCl upon microwave irradiation to produce 2-hydroxy quinoline-3-carbaldehyde (IIa, b). Subsequent treatment with various substituted hydrazides produced the new Schiff bases of quinoline III (a-f). TLC and melting point were used to assess the synthesised compounds' purity. Using spectral analyses including infrared, 1H NMR, and mass spectroscopy, the structure of every freshly synthesised molecule was verified. Antibacterial and anthelminthic properties were investigated for each synthesised molecule. The compounds IIIb and IIIc had good effectiveness against both Gram-positive and Gram-negative bacteria, according to the data. All of the organisms were moderately active against compounds IIb and IIIf. However, when compared to the common medication amikacin, none of the compounds have demonstrated as much antibacterial efficacy. The anthelminthic activity of compounds IIIe and IIIf was moderate, while that of compounds IIIa and IIIc was good. But when compared to the common medication albendazole, none of the substances have demonstrated as much anthelmintic activity. According to the study, substances that contain quinoline derivatives with an acridine moiety have antibacterial action against Salmonella typhi, Pseudomonas aeruginosa, Bacillus subtilis, Bacillus cereus, Staphylococcus epidermidis, and Klebsiella pneumoniae. These compounds have good anthelmintic action as well. The green synthesis method mentioned above might be the best option for future industrial uses as well as medical requirements.

Keywords: *Quinoline, Anthelminthic, Antibacterial, Albendazole, Amikacin*

1. INTRODUCTION

The frequency of potentially fatal infections caused by gram-positive, gram-negative, and fungal bacteria has increased dramatically in recent years. These are regarded as one of the major worldwide health issues of the twenty-first century. The effectiveness of currently available treatments is drastically reduced as a result of rapidly emerging drug-resistant infections. [1] A report from 2024 states that antibiotic resistance kills one million people year worldwide, and by 2050, that number is predicted to increase to 10 million. [2] Fungal infections also pose a threat to human health, especially for those with weakened immune systems. [3–5] Over 90% of potentially fatal invasive fungal infections (IFI) are caused by species of Aspergillus and Candida. [6] With a fatality rate of about 40%, Candida albicans is the most common cause of IFI and the fourth leading cause of nosocomial bloodstream infection in hospitals. [7–9] One important challenge in preventing these severe medical issues is the development of new antibacterial and antifungal medications. In order to replace or substitute current antibiotics, it is crucial to synthesise a new class of antimicrobial medicines with unique molecular structures and functions. Many researchers have been working on developing novel targets and structure-based drug design to introduce new chemotherapeutics that can overcome acquired resistance in recent decades. [10–12]

One of the most significant scientific fields in the pharmaceutical sector nowadays is the chemistry of heterocyclic compounds. F.F. Runge extracted quinoline from coal tar for the first time in 1834. It was separated as a degraded quinine and cinchonine product later in 1842. One of the most adaptable heterocyclic nuclei with nitrogen is quinoline (1-azanaphthalene). [13] Medicinal researchers have been interested in quinolines because they are an intriguing class of chemicals with a variety of pharmacological actions, such as anti-inflammatory [14], anticonvulsant [15], antitubercular [16], anticancer [17], antimalarial [18], antibacterial [19], including antiatherosclerotic, vasodilator, bronchodilator Klusa et al., and hepatoprotective activities [20, 21]. Prominent commercial medications containing quinoline nuclei include antiviral activity (Elvitegravir), antifungal activity (clioquinol), antibacterial activity (Norfloxacin, Ciprofloxacin), antimalarial activity (Chloroquine, Amodiaquine), and many more that are undergoing clinical studies. [22] Quinoline is a key component of medication research and discovery that has attracted a lot of interest. It was thought to be beneficial to create and synthesise specific biologically active molecules and test them for their antibacterial and anthelmintic properties in vitro and in-vivo in order to determine the medicinal significance of quinolone hybrids as a possible therapeutic agent.

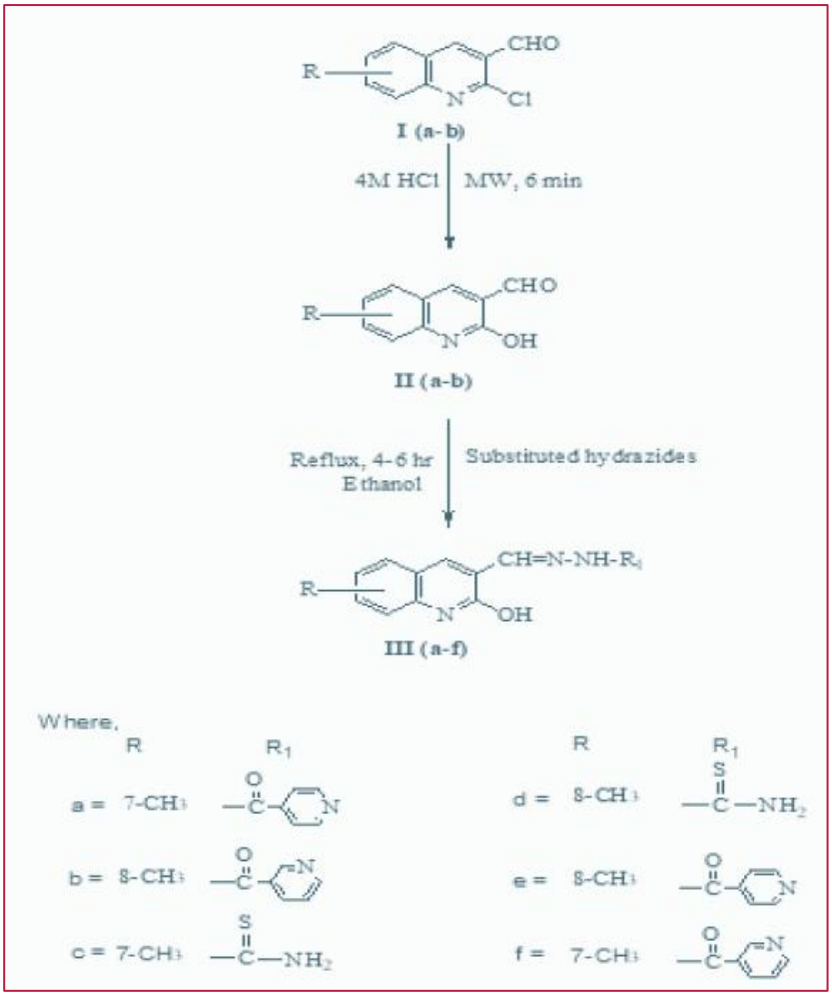
2. EXPERIMENTAL

Materials and Methods: Uncorrected melting points were measured in open capillary tubes. Thin-layer chromatography (TLC) on 0.5 mm thick silica gel-G plates was used to verify the compounds' formation, and iodine and UV light were used to identify the spots. Through recrystallisation using appropriate organic solvents, all molecules were purified. Using the KBr pellet technique, IR spectra were captured using a Brooker-ALPHA FT-IR instrument. The Shimadzu GC-MS-QP-2010 model was used to record mass spectra using the direct intake probe technique. With a Bruker AC-400 MHz spectrometer, 1H were measured in CDCl3 solution. Agilent thin layer chromatography was used to verify the synthesised compounds' purity. The outcomes align with the designated structures. The Euro EA 3000 elemental analyser was used to perform elemental analysis on all of the synthesised compounds, and the results match the allocated structures.

Synthesis of Quinoline derivatives

General Procedure for the Synthesis of 7/ 8-methyl-2-hydroxyquinoline-3-carbaldehyde II (a, b): For six minutes, a mixture of 7 or 8-methyl-2-chloro-3-formylquinolines (0.01 mol) and 30 millilitres of a 4M HCl solution were exposed to microwave radiation (120 W). As it cooled, a yellow solid precipitated. This was filtered, dried, and recrystallised from glacial acetic acid before being added to a beaker filled with 80 g of crushed ice. [23-25]

General procedure for the synthesis of compounds III (a-f): Compound II (a, b) (0.005 mol) was mixed with substituted hydrazides (0.005 mol) and glacial acetic acid catalytically in 25 millilitres of absolute ethanol. For six hours, the mixture was refluxed. After cooling the reaction mixture, a solid chemical was produced. The final compounds III (a-f) were obtained by filtering, drying, and recrystallising the combination of ethanol and DMF. [26-28]



Scheme 1: Synthesis of quinoline derivatives

Antibacterial activity: A significantly altered cup plate method was used to assess the synthetic compounds' antibacterial activity. The bacterial strains Salmonella typhi (MTCC 4211), Pseudomonas aeruginosa (MTCC 3622), Bacillus subtilis (MTCC 4332), Bacillus cereus (ATCC 4222), Staphylococcus epidermidis (ATCC 21322), and Klebsiella pneumoniae (ATCC 21643) were all grown on Muller Hinton agar. After each organism was suspended in a standard saline solution, a transmittance (T) of 75-77% at 530 nm—or 106 CFU/ml—was measured. DMSO was used to dissolve each test chemical at a dosage of 2 mg/ml. Twenty microlitres of the microbial suspension were added to each plate. [29-31] Each cup received 100 µl of the test chemicals. After the bacterial plates were incubated for 24 hours at 37°C, the growth inhibition zone was used to determine the positive antibacterial activity, which was then compared to the solvent as a negative control and amikacin as a comparative medication.

Anthelmintic activity: The anthelmintic activity of adult Indian earthworms (Pheretima posthuma) was investigated. To get rid of all the faeces, the earthworms that were gathered from the soils' waterlogged sections were cleaned with regular saline. For all experimental procedures, earthworms measuring 4-5 cm in length and 0.1-0.2 cm in width were employed. Because of their morphological and physiological similarities to human intestinal roundworm parasites, earthworms can be employed to investigate anthelmintic activity. The anthelmintic activity of the recently synthesised compounds was examined. For the current investigation, P. posthuma of almost equal size were chosen at random. Prior to research, the worms were acclimated to the laboratory environment. [32] Four sets of six earthworms each were created from the earthworms. As a standard, albendazole was diluted with regular saline solution to get 0.2% w/v and 0.5% w/v, which were then transferred into petri dishes. A little amount of DMSO was used to prepare the synthesised compounds, which were then diluted to create two concentrations: 0.2% w/v and 0.5% w/v for each product. The negative control was regular saline. For every concentration, six earthworms of roughly the same size are collected and kept at room temperature in petri plates. [33] The duration of total paralysis and death is noted. For every sample, the mean fatal time and mean paralysis time were computed. Each worm was regularly exposed to external stimuli that excite and generate movement in the earthworms, if they were alive, in order to determine death. The time it took for the worms to become motionless was recorded as the paralysis time. [34-35]

3. RESULTS AND DISCUSSION

7 or 8-substituted -2-hydroxy-3-formylquinolines I (a, b) have been reacted with substituted hydrazides to create a new series of 2-hydroxy quinoline derivatives III (a-f). TLC was used to verify the synthesised compounds' purity. All of the recently synthesised compounds' structures were verified by spectral and physicochemical data. Using Pheretima posthuma as test worms, all of the compounds were evaluated for their anthelmintic and in-vitro antibacterial properties using a modified cup plate method.

Table 1: Physical data of synthesized newer quinoline derivatives II (a -b) & 3 (a-f)

Derivatives	Chemical Formula	M.W	Composition C					M.P.(°C)
			C	H	N	O	S	
IIa	$C_{16}H_{12}NO_4$	282.65	57.65%	13.63%	11.20%	19.20%	-	256°C
IIb	$C_{17}H_{14}NO_4$	296.82	58.78%	4.06%	20.64%	18.42%	-	265°C
IIIa	$C_{17}H_{14}N_4O_2$	306.38	59.82%	11.46%	18.88%	12.65%	-	265°C
IIIb	$C_{17}H_{14}N_4O_3$	322.87	48.74%	9.07%	15.55%	14.23%	-	239°C
IIIc	$C_{17}H_{14}O_3S$	298.08	50.01%	7.46%	-	27.68%	7.85%	243°C
IIId	$C_{17}H_{14}N_4OS$	354.65	51.19%	5.82%	3.32%	15.15%	7.59%	255°C
IIIe	$C_{17}H_{14}N_5O_4$	352.54	45.55%	6.74%	19.17%	17.50%	-	249°C
IIIf	$C_{17}H_{14}N_5O_5$	384.98	49.85%	8.10%	3.08%	22.06%	-	275°C

Table 2: Physical and chemical properties of synthesized compound

Code	Colour	Rf value	% yield
IIa	White liquid	0.73	67.65
IIb	Off white liquid	0.72	60.32
IIIa	Pale yellow liquid	0.51	72.98
IIIb	Yellowish brown liquid	0.48	65.54
IIIc	Pale brown liquid	0.58	68.23
IIId	Yellowish brown liquid	0.67	58.76
IIIe	Off white liquid	0.56	63.11
IIIf	Off white liquid	0.54	64.73

Table 3: Spectral Analysis of Synthesized compound

Derivatives	IR (KBr) cm^{-1}	1H NMR (400 MHz, DMSO-d6, δ ppm)	Mass (m/z)
II a	3233.54 (OH), 1876.03 (C=O), 1733.14 (C=N)	2.18 (s, 3H, CH_3), 7.34 (d, 1H, C6-H of quinoline), 7.52 (d, 1H, C8-H of quinoline), 7.91 (d, 1H, C5-H of quinoline), 8.26 (s, 1H, C4-H of quinoline), 9.56 (s, 1H, CHO), 11.65 (s, 1H, OH).	282.65
II b	3232.54 (OH), 1895.52 (C=O), 1543.23 (C=N).	2.14 (s, 3H, CH_3), 7.11 (d, 1H, C6-H of quinoline), 7.39 (d, 1H, C8-H of quinoline), 7.59 (d, 1H, C5-H of quinoline), 8.21 (s, 1H, C4-H of quinoline), 9.34 (s, 1H, CHO), 11.14 (s, 1H, OH).	296.82
III a	3233.56 (OH), 3063.24 (NH),	2.45 (s, 3H, CH_3), 7.56 - 8.67 (m, 9H, C4, C5, C6, C8-H of quinoline, CH=N & C2, C3, C5, C6-H of pyridine), 10.65 (s, 1H,	306.38

	1986.43 (C=O), 1543.17 (C=N).	NH), 11.54 (s, 1H, OH).	
III b	3342.53 (OH), 3242.67 (NH), 1987.75 (C=O), 1553.64 (C=N)	2.17 (s, 3H, CH_3), 7.26 (s, 2H, C3 & C4-H of pyridine), 7.64 (s, 1H, C8-H of quinoline), 7.82 (s, 2H, C2 & C5-H of pyridine), 7.91 (s, 1H, C6-H of quinoline), 8.54 (s, 1H, C5-H of quinoline), 8.67 (s, 1H, CH=N), 8.88 (s, 1H, C4-H of quinoline), 10.55 (s, 1H, NH), 11.62 (s, 1H, OH).	322.87
III c	3342.53 (OH), 3231.54 (NH), 1696.11 (C=O), 1512.54 (C=N)	2.13 (s, 3H, CH_3), 7.65 (d, 1H, C8-H of quinoline), 7.87 (d, 1H, C6-H of quinoline), 8.24 (s, 1H, C4-H of quinoline), 8.43 (s, 2H, NH2), 8.75 (s, 1H, CH=N), 10.11 (s, 1H, NH), 11.55 (s, 1H, OH).	298.08
III d	3312.87 (OH), 3053.64 (NH), 1985.43 (C=O), 1564.21 (C=N)	2.54 (s, 3H, CH_3), 7.11 (d, 1H, C8-H of quinoline), 7.39 (d, 1H, C6-H of quinoline), 8.13 (s, 1H, C4-H of quinoline), 8.56 (s, 2H, NH2), 8.74 (s, 1H, CH=N), 10.86 (s, 1H, NH), 11.65 (s, 1H, OH).	354.65
III e	3321.54 (OH), 3122.54 (NH), 1911.65 (C=O), 1521.63 (C=N)	2.16 (s, 3H, CH_3), 7.56 (s, 2H, C3 & C4-H of pyridine), 7.56 (s, 1H, C8-H of quinoline), 7.53 (s, 1H, C6-H of quinoline), 7.32 (s, 1H, C5-H of quinoline), 9.11 (s, 1H, CH=N), 9.76 (s, 1H, C4-H of quinoline), 10.54 (s, 1H, NH), 11.04 (s, 1H, OH)	352.54
III f	3312.56 (OH), 3054.98 (NH), 1875.64 (C=O), 1543.23 (C=N),	2.53 (s, 3H, CH_3), 7.33-8.54 (m, 9H, C4, C5, C6, C8-H of quinoline, CH=N & C2, C3, C5, C6-H of pyridine), 9.32 (s, 1H, NH), 10.65 (s, 1H, OH	384.98

Antibacterial activity: Based on the results of the antibacterial screening, all of the compounds showed action against every organism used, as shown in Table 4. Both Gram-positive and Gram-negative bacteria have been demonstrated to be effectively inhibited by compounds IIIa and IIIb. All of the organisms were moderately active against compounds IIIa and IIIb. Out of all the synthesised compounds, compounds IIb and IIIf had the least amount of activity. However, when compared to the common medication amikacin, none of the compounds have demonstrated as much antibacterial efficacy.

Table 4: Antibacterial activity of newer quinoline derivatives containing acridine moiety

Derivatives	**Zone of inhibition (mm)**					
	B. subtilis	**B.cereus**	**S. epidermidis**	**S. typhi**	**P. aeruginosa**	**K. pneumoniae**
IIa	14	11	14	13	12	11
IIb	11	9	13	14	5	10
IIIa	10	8	13	12	11	10
IIIb	14	14	11	13	11	11
IIIc	12	14	11	10	10	12
IIId	11	9	9	8	12	9
IIIe	7	9	13	9	12	8
IIIf	11	10	10	11	11	13
NS	-	-	-	-	-	-
Amikacin	23	21	22	24	22	20

Anthelmintic activity: Table 5 displays the results of the compounds' anthelmintic activity on P. posthuma. At both doses,

compounds IIb and IIIb demonstrated good action, compounds IIIe and IIIf demonstrated moderate activity, and compounds IIIc and IIId demonstrated very little activity. But when compared to the common medication albendazole, none of the substances have demonstrated as much anthelmintic activity.

Table 5: Anthelmintic activity of newer quinoline derivatives

Compounds	**Time for paralysis (min)**		**Time for death (min)**	
	Percentage of concentration		**Percentage of concentration**	
	0.2%	**0.5%**	**0.2%**	**0.5%**
IIa	13.54	11.56	20	16
IIb	3.9	2.65	11	7
IIIa	16.56	10.53	29	18
IIIb	12.54	9.45	25	16
IIIc	39.65	23.65	59	34
IIId	7.54	5.75	16	11
IIIe	1.64	1.65	10	5
IIIf	7.55	8.65	24	18
Normal saline	-	-	-	-
Albendazole	0.32	0.21	0.38	0.31

Time of paralysis and death of worms in minutes in the control (normal saline). Values are expressed as mean ± SEM (n=5). Means significantly different at $p<0.05$ compared with albendazole treated group in each column using independent Student's t-test. SEM: Standard error of mean

Statistical analysis of anthelminthic activity: The independent Student's t-test was used for statistical analysis, and all data were displayed as mean ± standard error of the mean. $P<0.05$ indicates statistical significance and meantime.

4. CONCLUSION

To sum up, the production of more recent quinoline derivatives was accomplished. Seven or eight-substituted -2-hydroxy-3-formylquinolines I (a, b) have been reacted with substituted hydrazides to create a new series of 2-hydroxy quinoline derivatives III (a-f). The antibacterial and anthelminthic properties of each of the eight newly synthesised quinoline derivatives were assessed. According to the results, every component exhibited strong anthelminthic and antibacterial properties. For the production of newer quinoline compounds for additional bioevaluation, the study might be a useful matrix.

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