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Research Article

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Antimicrobial Evaluation of Some Newly Synthesized Terpolymer Resins Derived From Substituted Resorcinol Biuret and Furfural

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ABSTRACT

Some novel resins which have ion exchange properties and anti-microbial activities were synthesized by polycondensation reaction of substituted resorcinol, furfural and biuret using hydroxybenzoic acid as catalyst. The structures of these resins were conformed using various characterization techniques such as FTIR, H^1-NMR spectral data. The antibacterial screening against Escherichia coli, Proteus vulgaris, Bacillus substillis, staphylococcus and antifungal activity against Drechera halodes, Fusarium oxysporium of the resins were evaluated. It is found that Parachlorophenyl substituted based copolymer resin is more active than other resins.

Key words: Substituted resorcinol, Biuret, Furfural, resin and antimicrobial agents.

INTRODUCTION

For the past several years much attention has been focused on synthetic resins derived from hydroxyl aromatic compounds because of their use as antifungal (1-3) and antibacterial agents. Application of resins in all fields of life has been richly increased in recent years. Even though many researchers have synthesized more number of resins but there is a noteworthy demand to synthesize eco-friendly resins having some biological activities like antifungal and antibacterial resorcinol-acetophenone copolymer was prepared [4] by using trifluoroacetic acid as catalyst having some antimicrobial activity. Similarly, 2, 4-dihydroxybenzaldehyde oxime-formaldehyde polymers were synthesized [5] in the presence of oxalic acid as a catalyst. Literature survey reveals that antimicrobial activity of copolymer resin derived from 2, 2'-dihydroxybiphenyl, dithiooxamide and formaldehyde was studied [6]. Synthesis, characterizations, with antimicrobial activity of acrylic copolymers derived from 2, 4-dichlorophenylacrylate was studied by Patel and coworkers [7]. Terpolymers of salicylic acid, thiourea with trioxane and 2-hydroxy -4 methoxy acetophenone, thiourea with trioxane and p-hydroxybenzoic acid, melamine with formaldehyde have been reported in literatures [8-11].Recently hiwase et al have characterized p-hydroxybenzaldehyde-resorcinol-formaldehyde and p-hydroxyacetophenone-hexamine formaldehyde [12-13]. M. M. Jadhao and coworkers have prepared terpolymer resins containing 2, 2'- biphenol with urea, thiourea, guanidine and formaldehyde and reported their structure, thermal degradation studies, and ion exchange properties [14-18]. Substituted acetophenone based terpolymers, and p-hydroxybenzaldehyde oxime based terpolymers, Phenolic resin with lanthanides (III) and poly [(2-Hydroxy-4-methoxy benzophenone) ethylene] resin have been studied by various coworkers [19-22]. Since several years, we have been working on the synthesis of novel bio active resin materials [22-23). In this connection, we report

synthesis and antimicrobial activity of new resins which contain substituted resorcinol, furfural and biuret moieties within the framework.

EXPERIMENTAL SECTION

Methods:

Resin Synthesis

A mixture of monomer (0.01 mol 2,4 – DHPK) 2,4- Dihydroxyphenylketone, Biuret (0.01 mol ,BU) and Furfural (0.02 mol, FF) were taken in a R.B.flask.5ml of 5M HCl was added slowly to the reaction mixture. The contents were refluxed to 120 – 130 ^{0}C for 7-8 hours with periodical shaking. After completion of the reaction, the mixture was poured in to ice cold water, filtered and washed with hot water to remove unreached reactants. Finally, the product was washed with little alcohol, dried in vacuum and used for structural characterization, antimicrobial evaluation anion exchange studies

Anti bacterial Evaluation

The *in vitro* antibacterial activities of the compounds were assayed with two concentrations (600 and 900mcg/ml) in DMSO against Gram-positive bacteria and Gram-negative bacteria. The broth dilution method was recommended by the national committee for clinical laboratory standards**.** The dried discs were stored at 4^{0}C. Nutrient medium (beat extract, peptone glucose, agar 15gr and one litre distilled water) was sterilized at 45^{0}C. Two days old culture growth of Escherichia coli, Proteus vulgaris, Bacillus substillis and staphylococcus were added to the medium and poured into a sterilized petriplates and allowed to solidify. Paper discs containing test compounds were placed with sterile forceps and incubated at 37^{0}C for 2 days. Sensitivity was determined by measuring the zone of inhibition, which is the area around the disc that did not have bacterial growth and represented in terms of zone of inhibition diameter after conversion.

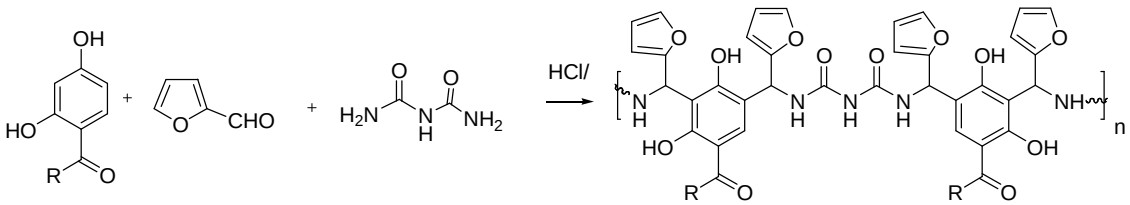
Antifungal Assay

The antifungal activity of resins was assyed by glass slide humid chamber technique as described by Horsfall. Monoscopic cultures of Drechera halodes and Fusarium oxysporium isolated from diseased fruits of tomato (lycopersicon esulentum) and maintained on Asthma and Hawkers medium. A mixture of glucose 5gr, potassium nitrate 3.5gr, potassium dihydrogen phosphate 1.7gr, magnesium sulphate 0.75gr, agar agar 15gr, and distilled water 1litre was employed for these studies Different concentrations of resins were prepared (as listed in table-1) by tube dilution technique. The spore suspension of different fungi was prepared in resin solution of different concentrations so as to appear 30-40 spores in high power microscope field. A drop of such solution was placed on a sterilized glass l side and 100% relative humidity was maintained by placing moistened sterilized blotter at the bottom of a petri dish and incubated at 27+ or – 2^{0}C for 8 hours. At the end of the incubation period, spores germinated and non-germinated were scored in 10 randomly selected microscopic fields so as to cover 350-400 spores. The percentage of spore germination inhibition was calculated

RESULTS AND DISCUSSION

The polycondensation reaction of 2, 4-Dihydroxy phenyl ketone (2, 4-DHPK) with Furfural (FF) and Biuret (BU) may be represented as follows

Structures



R= Me, ethyl, propyl, butyl, benzyle

Table-1: FT-IR Spectral data of newly synthesized resins

DHPK	OH & N-U	C=O	C=C	Bridge-CH-	Resorcinol phenyl
2,4DHPP	3360	1680	1635	1440	872
2,4DHPE	3380	1750	1625	1470	885
2,4DHPB	3387	1670	1620	1446	855
2, 4DHPPE	3340	1750	1610	1430	--
2,4DHPPE-PM	3460	1720	1580	1480	885
2,4DHP(PC)PE	3320	1745	1595	1450	870

Table-2; H^1 -NMR chemical shift values of newly synthesized resin copolymers

Co monomer code	Ter. C-H protons	Protons of ortho& urfuryl	Amide protons	Side Chain Protons	Other
2,4DHPE	6-31	7.8; 6.35-7.8	10.20	2.2	6.8
2,4DHPP	6.32	7.9; 6. 4-7.9	10.10	2.5 & 1.4	6.7
2,4DHPB	6.32	7.8; 6.5-7.8	10.0	2.2,1.5,1.2	6.2
2, 4DHPPE	6.35	7.6; 6.8-7.8	10.2	2.4,1.3	6.4
2,4 DHP(PM)PE	6.29	7.7; 6.9-7.8	10.3	2.3,1.2,1.3	6.5
2,4 DHP(PC)PE	6.35	7.6;6.4-7.6	10.2	2.2,1.3	6.8

Table-3: Physicochemical properties of newly synthesized resins

Entry	Co monomer	Reaction Time	M.P	Colour	Yield
1	2,4DHPE	2	350	LIGHTblack	65
2	2,4DHPP	1.5	330	black	60
3	2,4DHPRE	2.5	250	black	68
4	2, 4DHPPE	2.75	260	Brownish-black	70
5	2,4 DHP(PM)PE	3	275	Light black	75
6	2,4 DHP(PC)PE	5.6	280	black	80

Table-4: Solubility characterization of newly synthesized resins

Comp code	MeOH	acetone	Solubility				
			Ethylacetate	$CHCl_3$	1,4 Dioxane	THF	C_6H_6
DHPE	(+)	(+)	(-)	(+)	(+)	(+)	(δ^+)
DHPP	(+)	(+)	(-)	(+)	(+)	(-)	(-)
DHPB	(+)	(+)	(+)	(+)	(+)	(+)	(-)
DHPPE	(δ^+)	(+)	(-)	(+)	(-)	(-)	(δ^+)
DHP(PM)PE	(δ^+)	(+)	(-)	(+)	(-)	(-)	(-)
DHP(PC)PE	(δ^+)	(δ^+)	(-)	(δ^+)	(-)	(-)	(δ^+)

Table-5: Bacterial properties of Resin Copolymer

Name of the copolymer resin	Amount Mg/disc	Zone of Inhibition Diameter(mm)			
		E-coli	p-vulgaris	B- subtillis	St-lbus
DHPE	600	3.8	3.24	3.14	4.00
	900	1.12	4.00	3.23	4.13
DHPP	600	2.12	6.24	2.13	3.13
	900	3.12	6.34	3.34	4.34
DHPB	600	2.25	7.81	2.21	3.23
	900	3.10	8.24	2.34	4.22
DHPPE	600	4.34	6.25	2.27	4.40
	900	5.14	5.15	3.12	4.12
DHP(PM)PE	600	5.21	3.14	2.36	3.16
	900	6.12	4.12	2.12	4.12
DHP(PC)PE	600	7.34	8.60	7.10	4.27
	900	9.36	8.25	7.34	5.37

Table-6: Fungicidal (Antifungal) activity of newly synthesized copolymer resins

Co polymer resin	Conc (Mg/ml)	% of spore germination inhibition	
		D- Halodes	F-Oxysporum
2,4-DHPE-FF-BU	160	41.3	50
	320	50.1	59.7
	480	59.2	69.2
	640	69	97.2
2,4-DHPP-FF-BU	160	45.2	54
	320	48.2	60.2
	480	58	70
	640	76.2	85.2
2,4-DHPB-FF-BU	160	47.2	55.2
	320	50.2	63.1
	480	55.5	80.2
	640	70.2	91.2
2, 4-DHPPE-FF-BU	160	48	57
	320	54	73
	480	61	81
	640	73.2	90
2,4- DHP(PM)PE-FF--BU	160	48	56
	320	61	67
	480	73	80
	640	96	90
2,4 DHP(PCl)PE-FF-BU	160	61	62.1
	320	71	72
	480	82	85
	640	91	92
Std Chlorimazole	160	45	51
	320	72	71
	480	76	80
	640	90	81
Control DMSO	NA	NA	NA

In the IR spectrum of resins a broad band appearing in the region of 3320-3360cm^{-1} may be assigned to stretching vibrations of phenolik –OH groups. The band at 1602 cm-1 may be attributed to an aromatic ring. The presence of methylene bridge (-CH_2-) in the polymeric chain may be allocated to the presence of a band at 1460-1430, cm^{-1}. The band at 1680-1750 cm-1 may be due to >C=O stretch of the resins. The bands obtained in the range 937 cm-1, 1074.46 cm-1 and 1123.45 cm-1 confirms the 1,2,3,5 substituted aromatic rings. (Table-1)

NMR spectral data of resins were shown in table 2. These spectra show a multiple signal (asymmetrical pattern) in the region 7.6 to 7.8(∂) ppm, which are due to aromatic protons. The signal appearing in the region 1.2 to2.5 (∂) ppm can be assigned to the proton of the side chain A signal at 9.2(∂) ppm shows intermolecular hydrogen bonding of the –NH- group or intermediate proton exchange reaction of both phenolic –OH groups . A weak signal at 10.2-10.5 (∂) ppm may be due to protons of the –NH- bridges. The solubility behavior of the resins was determined by using solvents of varying solubility parameters. The resins were soluble in DMSO, chlorophom, and sparingly soluble in methanol and ethanol, however all the resins were in soluble in water. All the synthesized resins showed high decomposition temperature. Antibacterial activity of the resins showed that the resins varied significantly in their antibacterial activity.. The antibacterial activities of the terpolymer were screened on various bacteria at these concentrations. Some of the synthesized resins have shown excellent antibacterial activities as compared to the standard Ciprofloxacin [24-27].Almost all resin; copolymers have shown moderate to good activity. The resin which has chloro-substitution has shown better activity than all other resins. The resins with DHPE and DHPPE have shown poor activity against E.Coli and B.Subtillis antibacterial activity of the resins under study could be referred to number of causes like injurious effect on the cell wall or cell division. Effect on permeability of cell membrane and cell enzyme system, chelating and precipitation of chemicals. Oxygen and Nitrogen atoms present in the resin can act as hydrogen acceptor in the metabolic system and by doing so disturb the normal hydrogenation and dehydrogenation reactions in the cell. This might be a reason for the high activity of the resins. In case of some other resins, a synergistic structural effect may be playing role in antibacterial activity and no single factor may be responsible for such activity. All synthesized resins showed moderate to better fungal activity against both D.Halodes and F.oxysporum. The monomer substitution in combination with other part of the resin was responsible

for antifungal activity. The chloro substituent resin was more potent antifungal agent. Many parameters may influence the antifungal activity, modification of biocidal group during interaction with fungi, acidity or alkalinity of the medium hardness of water etc.

CONCLUSION

The resins showed excellent antimicrobial activities as compared to standard drugs. The synthesized terpolymer resins may find variety of applications in the field of material science. The present antimicrobial investigation may serve as a guide for designing new biocidal coating that has the advantage of being non-polluting.

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