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Research Article

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Synthesis, antimicrobial and ion exchange studies of some terpolymer resins derived from substituted resorcinol, biuret and formaldehyde

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ABSTRACT

The novel resins were synthesized by polycondensation reaction of substituted resorcinol, formaldehyde and biuret using HCl as catalyst. The structures of these resins were studied using various characterization techniques such as FTIR, ^{1}H-NMR spectral data. The antibacterial screening against Escherichia coli, Proteus vulgaris, Bacillus substillis, Staphylococcus and antifungal activity against Drecherahalodes, Fusarium oxysporium of these resins were also evaluated. It is found that parachlorophenyl substituted based copolymer resin is more active than other resins. Similarly, acid catalyzed terpolymer resins were found to be more potent than base catalysed resins.

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

INTRODUCTION

The human civilization is based on the materials they use in their daily life. Likewise the history of time frame has been classified into Stone age, Copper age and Bronze ages. The present time is sometimes knows as plastic age in view of wide spread use of these materials, a situation which has developed rapidly over last 70 years. The rapid increase in the range of manufactured products resulted directly from the development of a broad range of new fibbers, plastics, elstomers, adhesives, resins and sealing materials in dental therapy. The biological essay of the resins evaluated and found to be highly sensitive to the bacteria and fungi. Most of the resins derived from substituted resins were shown to be selective ion exchangers for certain metal ions [1-5].

Synthetic resins derived from dihydroxy/ hydroxyl amino/halo hydroxyl aromatic ketones or aromatic carboxylic acids have been attracted the attention of many research workers in the recent years, because of their versatile use as ligands, ionoc exchangers, thermal stable compounds, bacteriocidal, fungicidal activities [6-8]. The terpalymeric resins which are made by poly condensation of substituted resorcinol/ substituted benzoicacid, biuret and farmaldihyde/furfural are expected to poses maximum ionic exchanges, sensitive for bacterial and fungal agents [9-12]. These reasons attracted us to synthesis novel terpolymeric resins from substituted resorcinol/substituted benzoicacid and biuret using formaldehyde/furfural as condensing agents in the presence of acid catalyst (HCl).

EXPERIMENTAL SECTION

Resin synthesis:

A mixture of monomer (0.01 mol 2,4 – DHPK) 2,4- Dihydroxyphenylketone, Biuret (0.01 mol BU) and Formaldehyde (0.02 mol) was taken in a round bottom flask.2ml of 5M HCl was added slowly to the reaction mixture. The contents were refluxed to 100 – 120 ^{0}C for 6-8 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 unreacted reactants. Finally, the product was washed with alcohol, dried in *vaccum* and used for structural characterization followed by antimicrobial evaluation.

Antibacterial Test:
Antibacterial sensitivity of the copolymer resins were monitored by the diffusion test. The disc diffusion method uses whatman filter paper discs 5mm in diameter, changed with appropriate amount of the test compound. The dried discs were stored at 4^0C. Nutrient medium (beat extract, peptone glucose, agar 15gr and one liter distilled water) was sterilized at 45^0C. 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 37^0C 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. Test chemicals were employed at two concentrations, 600 and 900mg/disc in DMSO. Simultaneously, blank sterilized filter paper discs impregnated with the solvents were used as control (Table 5).

Antifungal assay:
Monoscopic cultures of Drecherahalodes and Fusarium oxysporium isolated from diseased fruits of tomato (lycopersiconesulentum) and maintained on Asthama 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. The antifungal activity of resins was assayed by glass slide humid chamber technique as described by Horsfall. Different concentrations of resins were prepared (as listed in Table 6) by tube dilution technique. The spore suspension of different fungi was prepared in resin solution of different concentrations so as to appear30-40 spores in high power microscope field. A drop of such solution was placed on a sterilized glass slide and 100% relative humidity was maintained by placing moistened sterilized blotter at the bottom of a petri dish and incubated at 27+ or – 2^0C 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 with the help of the formula, Percentage of spore germination inhibition = Percentage of spore germination in treated X 100 / Percentage of spore germination in control Water in place of resin solution served as control. The experiment was conducted three times, since the difference among replicators was insignificant. Average of three replicates was recorded to calculate the percentage of the spore germination inhibition.

RESULTS AND DISCUSSIONS

The polycondensation reaction of 2,4-dihydroxy phenyl ketone (2,4-DHPK) with formaldehyde (FM) and biuret may be represented as shown in scheme 1.

Scheme 1:

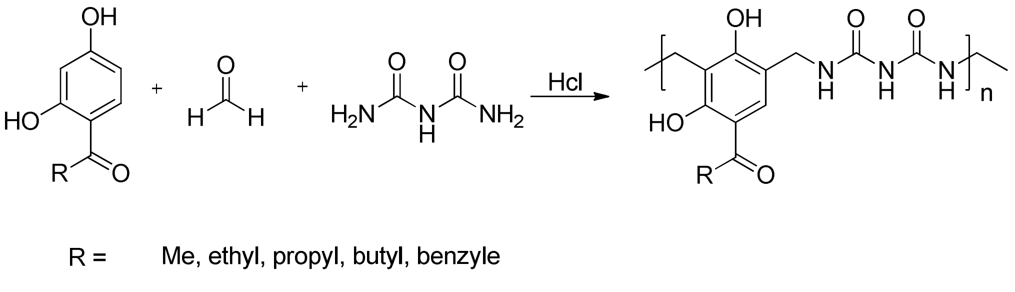

Table-1: FTIR Spectral data of newly synthesized resins

DHPK	OH & N-U	C=O	C=C	BRIDGE -CH2-	Resorcinol phenyl
2,4DHPP	3380	1690	1625	1440	870
2,4DHPE	3390	1720	1620	1472	880
2,4DHPB	3397	1650	1610	1456	850
2, 4DHPPE	3440	1720	1600	1438	--
2,4 DHPPE-PM	3470	1730	1590	1490	880
2,4 DHP(PC)PE	3220	1740	1590	1440	872

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

Comonomer	Bridged protons	Ortho proton	Amide protons	Side chain protons	Other
2,4DHPE	4-36	7.8	10.2	2.2	6.8
2,4DHPP	4.29	7.9	10.1	2.5 & 1.4	6.7
2,4DHPB	4.29	7.8	10.0	2.2,1.5,1.2	6.2
2, 4DHPPE	4.35	7.6	10.2	2.4,7.3	6.4
2,4 DHP(PM)PE	4.29	7.7	10.3	2.3,7.2,1.3	6.5
2,4 DHP(PC)PE	4.35	7.6	10.2	2.2,7.3	6.8

Table-3: Physico chemical properties of newly synthesized resins

Entry	Comonomer	Reaction time	M.P (°C)	Colour	Yield
1	2,4DHPE	2	350	Light yellow	65
2	2,4DHPP	1.5	330	Light yellow	60
3	2,4DHPRE	2.5	250	Light yellow	68
4	2, 4DHPPE	2.75	260	Light yellow	70
5	2,4 DHP(PM)PE	3	275	Light yellow	75
6	2,4 DHP(PC)PE	5.6	280	Light brown	80

Table-4: Solubility characterization of newly synthesized resins

Comp code	Solubility							
	MeOH	Acetone	Ethylacetate	$CHCl_3$	1,4 Dioxane	THF	C_6H_6	H_2O
DHPE	(-)	(+)	(-)	(+)	(+)	(-)	(δ^+)	(-)
DHPP	(δ^+)	(+)	(-)	(+)	(+)	(-)	(-)	(-)
DHPB	(δ^+)	(+)	(δ^+)	(+)	(+)	(-)	(-)	(-)
DHPPE	(-)	(+)	(-)	(+)	(-)	(+)	(δ^+)	(-)
DHP(PM)PE	(-)	(+)	(-)	(+)	(+)	(-)	(-)	(-)
DHP(PC)PE	(-)	(+)	(-)	(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-albus*
DHPE	600	2.8	3.14	3.24	4.12
	900	1.25	4.10	3.12	4.00
DHPP	600	NA	7.24	2.23	3.12
	900	NA	6.12	3.24	4.16
DHPB	600	2.15	8.61	2.17	3.40
	900	3.20	8.16	2.11	4.12
DHPPE	600	4.12	6.29	1.27	4.21
	900	5.24	4.15	2.76	5.14
DHP(PM)PE	600	7.21	3.14	2.36	3.16
	900	6.12	4.12	2.12	4.12
DHP(PC)PE	600	8.34	9.60	8.12	4.12
	900	10.36	8.12	7.16	5.14
ciproflaxasine	600	3.15	4.50	4.50	4.55
	900	5.00	4.45	4.00	5.00
Control DMSO		NA	NA	NA	NA

All the resin copolymers were characterized by FTIR and ^{1}H-NMR spectra. The spectral data and assignment of all the resin copolymers were given in Table 1and Table 2. The solubility behaviors of the resins were determined by using solvents of varying solubility parameters. The resins were soluble in1,4 Dioxane, acetone,chloroform. Sparingly soluble in methanol, ethyiacetate, benzene and however all the resins were in soluble in water. All the synthesized resins showed high decomposition temperature.

An observation of Table 5antibactrial activity of the resins showed that the resins varied significantly in their antibacterial activity. 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, chelation 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-HalodesAnd F.oxysporum. These copolymer resins showed more than 50% inhibition of spore germination of both the fungi under investigation even at 160mg/ml concentration. F.oxysporum was relatively more sensitive than D-Halodesas the percentage inhibition was more than 60 even at 160 mg/mL concentration.

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-FM-BU	160 320 480 640	42.3 52.4 60.2 70.4	52.3 60.4 70.2 98.2
2,4-DHPP-FM-BU	160 320 480 640	44.2 49.2 60.2 70.2	54.2 62.2 72.2 92.0
2,4-DHPB-FM-BU	160 320 480 640	48.0 52.2 60.4 73.2	59.0 64.0 80.1 92.2
2, 4-DHPPE-FM-BU	160 320 480 640	49.0 53.2 62.2 74.0	57.0 72.2 82.0 90.2
2,4- DHP(PM)PE-FM-FM-BU	160 320 480 640	49.2 60.2 74.4 97.2	58.0 68.4 82.2 92.2
2,4 DHP(PCl)PE-FM-BU	160 320 480 640	60.2 76.3 88.2 98.0	60.4 72.2 84.0 94.0
StdChlorimazole	160 320 480 640	50 70 80 95	55 72 85 90
Control DMSO		NA	NA

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 paramerers may influence the antifungal activity, modification of biocidal group during interaction with fungi, acidity or alkalinity of the medium hardness of water etc.,the present antimicrobial investigation may serve as a guide for designing new biocidal coating that has the advantage of being non-polluting. In conclusion, these resin copolymers are excellent materials for purification of water because these have both antimicrobial activity and ion exchange properties.

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