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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF SOME AZO-COMPOUNDS

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Abstract

Two azo-compounds, azobenzene-4, 4'-dicarboxylic acid1 and 4-(2-hydroxy-naphthalen-1-ylazo)-benzoic acid2 were synthesized for study of their antibacterial activity. Structures of the two compounds were confirmed by NMR, IR and elemental analysis.Antibacterial activity the compounds was tested by disk diffusion method against the bacteria strains Staphylococcus aurous and Escherichia coli. The compound 1was moderat tive while 2 was highly active against all the bacteria species tested.

Key words

Azo-compounds; antimicrobial activity;disk diffusion method

Introduction

Azo compounds are the largest and the most versatile class of compounds. They possess intense bright colors, in particular oranges, reds and yellows. Design and synthesis of new azo compounds have been increasing greatly in the past few decades owing to their extensive applications in the field of heterogeneous catalysis (Fujita et al., 1994), gas storage (Cheon & Suh, 2009), separation (Kosalet al., 2002), ion exchange (Moris, & Wheatley, 2008), and sensing applications(Mir et al., 2010).In the recent time, azo compounds have attracted a great deal of attention as a number of these compounds have been recognized to act as models for biologically relevant species (El-Sonbati et al., 2013; El-Sonbati et al., 2014; Diab et al., 2013).

Since compounds with azobenzene and azophenol moiety have been reported to exhibit biological activities independently (Mkpenie et al., 2008; Piottoet al., 2017) it is therefore obvious that azo compounds having both azo and phenolic group will show a higher biological activity.Biological activity of azobenzene moiety results from enzyme-mediated reduction of the azo bond that occurs in vivo (Rinde & Troll, 1975) while the biological activity ofazophenol moiety is due to making of H-bond between –OH group

and target receptor (Piotto et al., 2017).

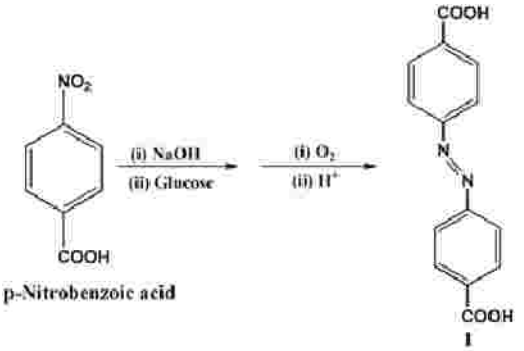
The present work involves synthesis of two azo compounds, one containing azobenzene moiety while the other containing azophenol moiety. It also includes characterization and antimicrobial studies of the two synthesized compounds.

Experimental section

All reagents and solvents were commercially available and used as received. The compounds1(Ghosh et al., 2008)and 2 (Furniss et al., 1989) were synthesized following reported methods. The carbon, nitrogen, and hydrogen contents of the compounds were determined by Carbo-Erba elemental analyzer 1108. The infrared spectra of the compounds were recorded on a Varian 3100 FT-IR spectrometer (4000–400cm–1) using KBr disks.1H and 13C NMR spectra of compounds were recorded using JEOL AL 300 MHz spectrometer.

Synthesis of azobenzene-4, 4'-dicarboxylic acid1: For the synthesis of 1, p-Nitrobenzoic acid (15 g, 67.5 mmol) and NaOH (50 g, 1.25 mmol) were mixed in water (225 mL), and the solution was heated on a water bath until the solid dissolved; hot aqueous glucose (100 g in 150 mL of water) was then added slowly into the above mixture at 50 °C whereupon a yellow precipitate was obtained, which immediately changed to a brown solution upon further addition of glucose. This reaction was highly exothermic. Then, a stream of air was passed into the mixture for 3h and a light brown precipitate was obtained. This was filtered, dissolved in water, and acidified with acetic acid (25 ml) whereupon a light pink precipitate was obtained. This was filtered, washed with plenty of water (300 mL), and dried in a desiccator to obtain 1 as a brownish orange powder. The analytical data of the compound 1 are as follows: Brownish orange solid, yield 80%, m.p. 335 °C, IR (KBr) vcm-1: 1683(C=O), 1600(N=N); 1H NMR(CDCl3) δ: 13.3 (2H, s, COOH), 8.16 (4H, J= 8.4 Hz, d, Ar), 8.01 (4H, J= 8.1 Hz, d, Ar); 13C NMR (CDCl3) δ: 166(COOH), 154(Ar), 133(Ar), 130(Ar), 122(Ar); analysis for C14H10N2O4: 58.53(58.34), 4.06(4.53), 11.38(11.04).

Scheme 1. Synthetic strategy of 1



p-Nitrobenzoic acid

1

Synthesis of 4-(2-hydroxy-naphthalen-1-ylazo)-benzoic acid2: For synthesis of 2, p-aminobenzoic acid (7.29mmol,1g) was dissolved in 5ml of 5N aqueous HCl solution and cooled to 0-5°C in an ice bath. The ice-cold solution of NaNO2 (7.29mmol,0.5g) in 2.5ml of water was added dropwise to the reaction mixture to obtain a diazonium salt. After complete addition, the resultant mixture was left in an ice bath for 1h with occasional stirring followed by the addition of β-napthol (7.29mmol,1g) dissolved in 10% NaOH solution and then cooled to 0-5°C. The reaction mixture was further stirred for 4h and then filtered. The residue was washed comprehensively with water and then recrystallized from H2O/ DMF (4:1).

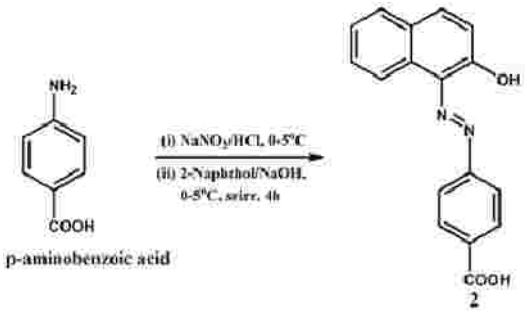
The analytical data of the compound 2 are as follows: Reddish brownsolid, yield 75%, m.p. 278°C, IR (KBr) vcm^{-1}:3375 (Phenolic-OH), 1681 (C=O, acid), 1601(N=N) ; 1H NMR(CDCl3) δ:15.87 (s, 1H, OH), 12.97 (s, 1H, COOH), 8.46 (d, 1H, J=7.8 Hz, naphthyl), 8.05 (d, 2H, J= 8.1 Hz , phenyl), 7.91 (m, 3H, 1H naphthyl and 2H phenyl), 7.74 (d, 1H, J= 7.2 Hz, naphthyl), 7.61 (t, 1H, J= 6.9 Hz, naphthyl), 7.47 (t, 1H, J= 6.9 Hz, naphthyl), 6.79 (d, 1H, J=9.6 Hz, naphthyl); 13C NMR (CDCl3) δ:171.64 (COOH), 160.89 (C-N=N, phenyl), 151.41(C-

Table 1: Antimicrobial activity of 1and 2

Bacteria	Inhibition Zone Diameter (mm)			
	Chloramphenicol	Ceftriaxone	Compound 1	Compound 2
Staphylococcus aureus	14	24	15	25
Escherichia coli	15	27	16	26

OH), 140.45(C-N=N, naphthyl); analysis for C17H12N2O3: 69.86(70.12), 4.14(4.50), 9.58(9.74).

Scheme 2. Synthetic strategy of 2



Antimicrobial studies of 1 and 2: The compounds 1 and 2 were screened in-vitrofor the presence of antimicrobial activity against twomicroorganisms: Staphylococcus aureus and Escherichia coliusing disk diffusionmethod (Goksuet al., 2005). The test compounds were dissolved in ethanol to give 10 mg/ 3 mL solutions. 20 µL solutions of these were applied to sterile disks and placed on nutrient agar plates with the bacteria. The plates were incubated for 24 hours and the zones of inhibition weremeasured. Ceftriaxoneand chloramphenicol were used as reference antibiotics. Table 1shows that the CLSI (Clinical and laboratory standards Institute) standards were used for antimicrobial susceptibility testing (CLSI, 2013). Ethanolshowed no inhibition zones on all the bacteria tested.

Results and discussion

The infrared spectra of 1 and 2 show peaks at 1683 and1681 cm-1 due to C=O stretching vibrations. The peaks at 1600 and 1601 cm-1 correspond to N=N stretching vibrations of 1 and 2. 1H NMR spectra exhibit peaks at δ = 13.3 and 12.97 ppm due to COOH proton of 1 and 2 respectively. The peak at δ = 15.87 in1H NMR spectra of 2 corresponds to OH(phenolic) proton.13C NMR spectra of 1 and 2 exhibit peaks at δ = 166 and 171.64 ppm due to COOH carbon respectively.

The test results of antibacterial activity are presented in Table 1. Chloramphenicol showed inhibition zones 14 mm for Staphylococcus aureusand 15 mm for Escherichia coli. Another antibacterial substance ceftriaxone showed inhibition zones 24 mm and 27 mm for Staphylococcus aureusandEscherichia colirespectively. The compound 1with inhibition zones 15 mm for Staphylococcus aureusand 16 mm for Escherichia coliwas moderately active while the compound 2 with inhibition zones 25 mm for Staphylococcus aureusand 26 mm for Escherichia coli was highly active.

Conclusion

The azo compounds1and2 were obtained from p-Nitrobenzoic acid and p-Aminobenzoic respectively. The compounds have been characterized by NMR, IR and elemental analysis. The compound 1 was moderately active while 2was highly active against the bacteria strains Staphylococcus aureus and Escherichia coli. This is most probably due to presence of only azo group in 1and both azoand phenol group in 2as compounds with azobenzene and azophenolic moiety have been reported to exhibit biological activities independently [Mkpenie et al., 2008; Piotto et al., 2017].

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