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SYNTHESIS OF DIAZO COMPOUNDS FROM AMINO BENZOPYRANO THIAZOLES

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ABSTRACT

8-Amino-6-chlorocoumarine (5) has been synthesized by multistep synthesis (by known literature methods) which involves the successive chlorination and nitration salicylaldehyde (1) to 5-chloro-3-nitrosalicyladehyde (3). The coumarin was synthesized by using Perkin reaction of 5-chloro-3-nitrosalicyladehyde. The nitro coumarin (4) obtained was reduced to 8-amino-6-chloro coumarin (5) which was then treated with bromine and potassium thiocyanate followed by the treatment of ammonia gives 2-amino-4-chloro-8*H*-chromeno-[8,7-*d*]-1,3-thiazol-8-one (6). The final 2-aminobenzo-1,3-thiazole derivative was diazotized and coupled with different phenols and anilines to yield diazo compounds. These compounds are then subjected to biological characterization.

Key Words: Coumarin, Thiazole, Perkin reaction, Diazo compounds, Salicyladehyde.

INTRODUCTION

Coumarin ring has an easy accessibility in the biological systems. Coumarin has varied useful properties[1]. Literature survey reveals the medicinal importance of coumarins derivatives, which cover the whole gamut of chemotherapeutic agents. It is hardly surprising that many biologically active synthetic coumarins derivatives have been patented. A collective bibliography of the relevant literature till 1936 is available in E. Merk's, Jahresbericht [2]. Natural coumarins daphnin in the plant protects, the plant from harmful effect of short wave radiations. Phytocidal action of coumarins to inhibit germination and root growth was reported[3] in nature in 1947. Some coumarins were found to be anthelmintic[4], calophyllolids, a complex coumarins isolated from calophyllum was found to show anti tubercular[5] activity. Coumarin acts as a growth regulator in number of plants.

Some polycyclic coumarins show anticarcinogenic properties[6,7]. Nitrogen mustards were synthesized[8] from 6-substituted coumarins as potential anticancer

agent. Some coumarins like 3-aminocoumarins; methoxy and hydroxyl derivatives of coumarins show antibacterial, antifungal activities[9-13]. Recently it was found that coumarins dye is used in optical recording medium. Coumarin dyes[14] at 0.0001-0.1% in lubricating oils intended for use in hydraulic fluids or coolants are extremely well suited for indicating or detecting leaks in hydraulic system and cooling system.

Coumarins also show cytostatic activity, antitumour[15], antioxidative and pro-oxidative effects[16], antimicrobial[17], antidiabetics[18], antileukemic[19], antiviral[20], antifungal[21,22] and various other activities. 2-Aminothiazoles have been reported[23-25] to possess pharmacological activity. Benzothiazole also possess antibacterial activity[26]. Aminocoumarins also exhibits antibacterial activity[27], we thought to combine both the moieties[28] to obtain 2-aminobenzopyranothiazoles.

Azo compounds play a prominent part in almost every type of application. Azo compounds are the most important class of synthetic colouring materials. The chemistry of azoic dyes has been given much attention by Dorman[4]. There are azo dyes available for the dyeing of cotton, wool, silk, linen, viscose rayon, distemper, printing ink etc. Azo dyes are also available for colouring foodstuffs and a few have valuable medicinal properties.

Azo compounds came to prominence in medicinal chemistry after the discovery that sulphanilamide, the active metabolite of the azo dye Prontosil Rubrum, had in vivo antibacterial properties. Despite being superseded by the penicillin antibiotics in most antimicrobial applications sulfa drugs such as sulphasalazine still find application in the treatment of Crohn's disease and ulcerative colitis[2]. The Sudan series of azo dyes, typified by Sudan I, are commonly used as microbial stains.

In the present work, novel azo compounds of 2-amino-4-chloro-8*H*-chromeno-[8,7-*d*]-1,3-thiazol-8-one and anilines & phenol are synthesized and check their antibacterial activities.

Experimental:

The 8-amino-6-chlorocuomarin has been synthesized by known literature methods. Salicylaldehyde (**1**) was chlorinated by using sulphuryl chloride give compound **2**. The compound **2** was nitrated by using fuming nitric acid and acetic anhydride gives compound 3. Compound **3** was heated with sodium acetate and acetic anhydride at 175^0C for about 8 hrs forming compound **4** which was reduced further by using calcium chloride and zinc powder gives compound **5** (8-amino-6-chlorocoumarin).

Synthesis of 2-amino-4-chloro-8*H*-chromeno-[8,7-*d*]-1,3-thiazol-8-one :

0.1 moles of 8-amino-6-chloro coumarin was placed in a 500 ml three neck round bottom flask fitted with a mechanical stirrer and surrounded by an ice bath. It is dissolved in 150 ml of 95% acetic acid. To this was added 0.6 moles of potassium thiocyanate dissolved in 150 ml of 95% acetic acid. A solution of 0.2 moles of liquid bromine in 20 ml of acetic acid was added slowly over a time span of one hour .The stirring and cooling was continued during addition. The stirring was continued for further one hour. The reaction mass was then poured in a beaker containing crushed ice and then neutralized with liquid ammonia. The solid obtained was filtered and dried at 70°C. The dry solid was dissolved in 100 ml of acetonitrile and insoluble solid particals were removed by filteration. The filterate was then evaporated on rotaevaporator to get the pure yellow coloured 2-amino benzopyranothiazole.

Diazotization of 2-amino-4-chloro-8*H*-chromeno-[8,7-*d*]-1,3-thiazol-8-one:

0.01 moles of 2-amino-4-chloro-8*H*-chromeno [8,7-*d*][1,3]thiazol-8-one was placed in a 250 ml three neck round bottom flask fitted with a mechanical stirrer, thermometer and the flask was surrounded by an ice-salt bath. The compound was dissolved in 25ml of hydrochloric acid and cooled to 0°C to 5°C. 0.01 moles of $NaNO_2$ dissolved in 5ml of water and chilled to 0 to 5°C and added slowly to the reaction flask with stirring. The temperature was maintained between 0 to 5°C. The stirring was continued for 10 minutes more.

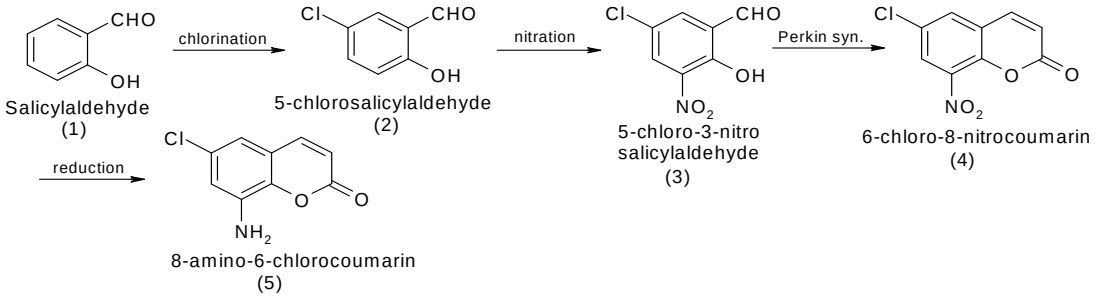
a. Coupling with Phenols:

In another 250 ml three neck round bottom flask fitted with a mechanical stirrer, thermometer and surrounded by an ice-salt bath, was taken 0.01 moles of compound to be coupled. It was dissolved in 150ml of dilute sodium hydroxide. The temperature was maintained between 0 to 5°C and the above diazotized mass was added slowly under stirring. The stirring was continued for another one hour. This mass then poured in a beaker containing crushed ice. The solid obtained was filtered and dried at 50°C and then crystallized from proper solvent.

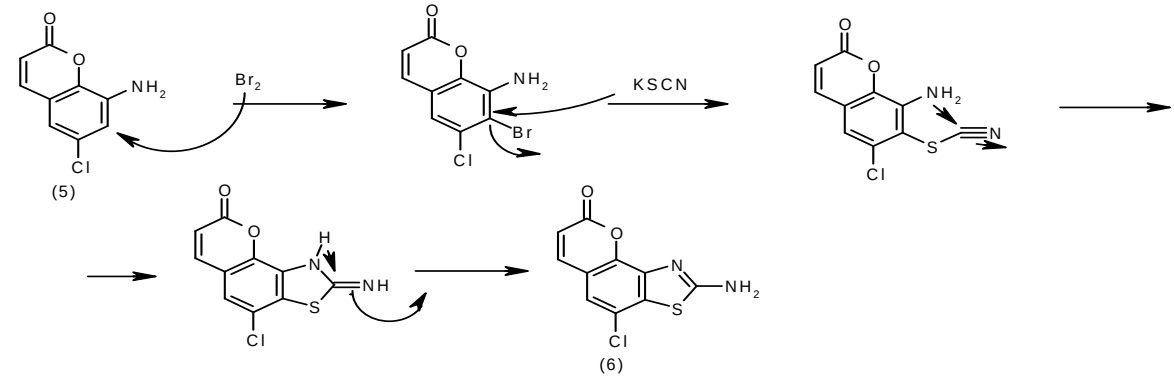
b. Coupling with Anilines:

In another 250 ml three neck round bottom flask fitted with a mechanical stirrer, thermometer and surrounded by an ice-salt bath, was taken 0.01 moles of compound to be coupled. It was dissolved in 150ml of Ethanol. The temperature was maintained between 0 to 5°C and the above diazotized mass was added slowly under stirring. The stirring was continued for another one hour. This mass then poured in a beaker containing crushed ice. The solid obtained was filtered and dried at 50°C and then crystallised with proper solvent.

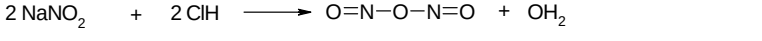
Scheme I: Synthesis of 8-amino-6-chloro coumarin from salicylaldehyde

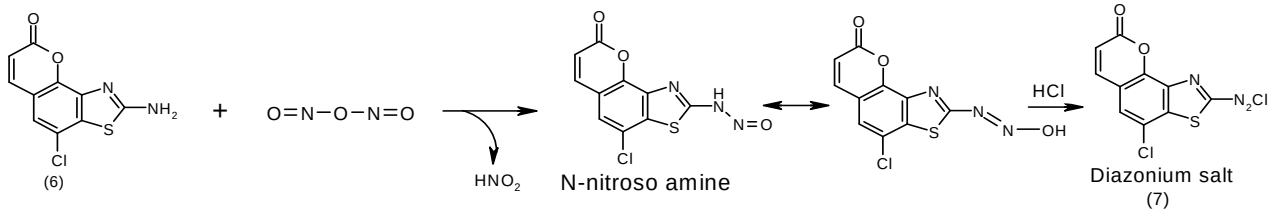


Scheme II: Synthesis of 2-amino-4-chloro-8H-chromeno[8,7-d](1,3)-thiazol-8-one (2-aminobenzopyranothiazole) (6)

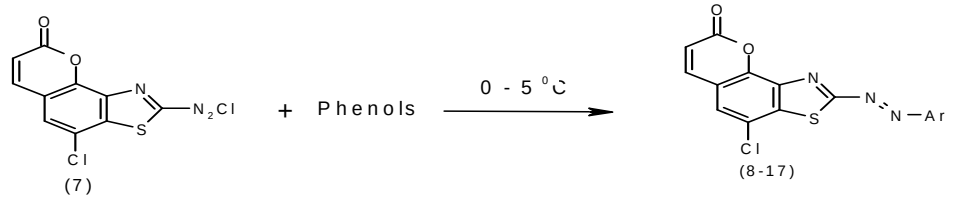


Scheme III: Diazotization of 2-amino-4-chloro-8H-chromeno[8,7-d](1,3)-thiazol-8-one (7)

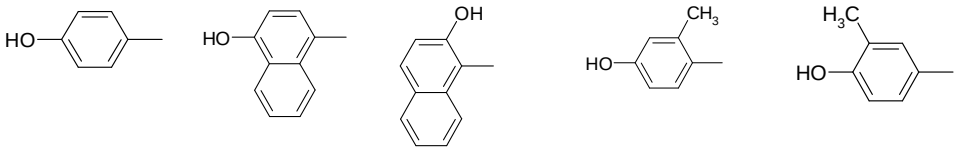




Scheme IV: Coupling of diazonium salt (7) with phenol

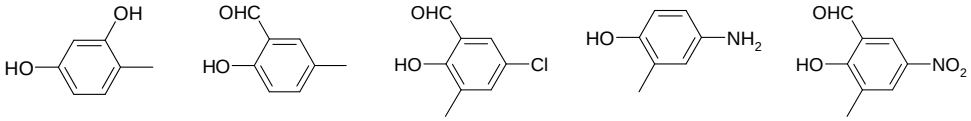


Ar-



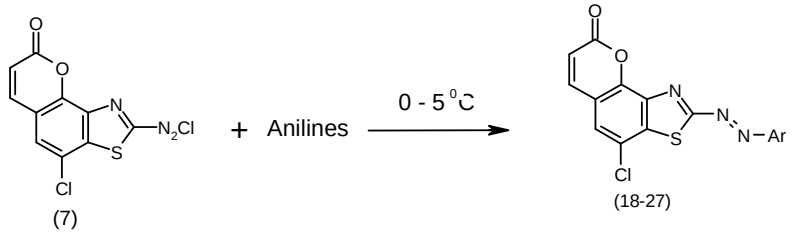
Product	**8**	**9**	**10**	**11**	**12**

Ar-



Product	**13**	**14**	**15**	**16**	**17**

Scheme V: Coupling of diazonium salt (7) with aromatic amines



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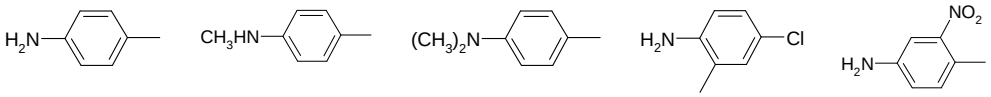
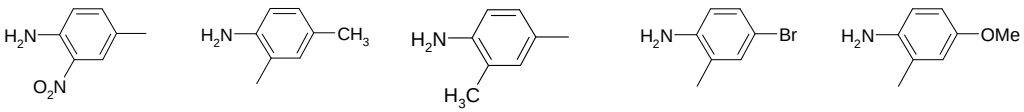


Product	**18**	**19**	**20**	**21**	**22**

Ar-



Product	**23**	**24**	**25**	**26**	**27**

Spectral Data :

8-amino-6-chloro coumarin (**5**). Straw yellow powder; yield 60%; M.p. 236°C; IR, ν cm^{-1}: 3485, 3381 (-NH_2 stretch), 1716 (-C=O stretch), 1562 (ring stretch), 1229, 1154, 1083 (-CH out of plane deformation), 833 (aromatic -Cl). Mass spectra: m/z = 195.4 $[M+H]^+$. Calculated for $C_9H_6NO_2Cl$: % C

55.26, H 3.09, Cl 18.12, N 7.16, O 16.36. Found C 55.12, H 3.13, N 7.24.

^{1}H NMR δ (in ppm): 5.775 (2H, bs, -NH_2); 6.470-6.502 (1H, d, Ar-Proton); 6.873-6.904 (2H, d, Ar-Protons); 7.880-7.913 (1H, d, Ar-Proton).

2-amino-4-chloro-8H-chromeno[8,7-d](1,3)-thiazol-8-one (6). Yield 65% and m.p. 180^{0}C.

IR, ν cm^{-1}: 3400, 3450 (-NH_2 stretch), 1775 (-C=O stretch), 1595 (ring stretch), 1100, 1150 (-CH out of plane deformation in aromatic), 833 (aromatic - Cl). Calculated for $C_{10}H_5N_2O_2SCl$: % C 47.53, H 1.99, S 12.69, N 11.09. Found C 47.47, H 1.97, N 11.13, S 12.80.

^{1}H NMR δ (in ppm): 4.688 (2H, bs, -NH_2); 6.607-6.641 (1H, d, Ar-Proton); 7.027 (1H, s, Ar-Protons); 8.237-8.269 (1H, d, Ar-Proton).

4-chloro-2-[(*E*)-(4-hydroxyphenyl)diazenyl]-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (8). Yield 72% and m.p. 160^{0}C.

IR, ν cm^{-1}: 3424 (-OH stretch), 3078 (-CH stretch), 1735 (-C=O stretch), 1577 (ring stretch), 1187, 1109 (-CH out of plane deformation in aromatic), 829 (aromatic - Cl).

^{1}H NMR δ (in ppm): 5.80 (1H, bs, OH); 6.54 (1H, d, Ar-Proton); 6.90 (2H, t); 7.40 (1H, s, Ar-Protons); 7.55 (2H, t); 8.10 (1H, d, Ar-Proton)

4-chloro-2-[(*E*)-(4-hydroxynaphthalen-1-yl)diazenyl]-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (9). Yield 50% and m.p. 245^{0}C.

IR, ν cm^{-1}: 3436 (-OH stretch), 3069, 2923, 2857 (-CH stretch), 1740 (-C=O stretch), 1593 (ring stretch), 1182, 1113 (-CH out of plane deformation in aromatic), 830 (aromatic - Cl).

^{1}H NMR δ (in ppm): 5.90 (1H, bs, OH); 6.52 (1H, d); 6.78 (1H, d); 7.34-7.39 (2H, m); 7.42 (1H, s); 7.68 (1H, d); 7.86 (1H, m); 8.08 (1H, d); 8.12 (1H, m).

4-chloro-2-[(*E*)-(2-hydroxynaphthalen-1-yl)diazenyl]-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (10). Yield 65% and m.p. 210^{0}C.

IR, ν cm^{-1}: 3434 (-OH stretch), 3080, 2929 (-CH stretch), 1749 (-C=O stretch), 1585 (ring stretch), 1195, 1180 (-CH out of plane deformation in aromatic), 847 (aromatic - Cl).

^{1}H NMR δ (in ppm): 6.735-6.766 (1H, d); 6.861-6.893 (1H, d); 7.502-7.552 (1H, t); 7.611-7.660 (1H, t); 7.719-7.745 (1H, d); 7.965-7.998 (1H, d); 8.417-8.450 (1H, d); 8.489 (1H, s); 8.571-8.598 (1H, bs).

4-chloro-2-[(*E*)-(4-hydroxy-2-methylphenyl)diazenyl]-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (11). Yield 50% and m.p. does not melt upto 250^{0}C.

IR, ν cm^{-1}: 3434 (-OH stretch), 3079, 2922, 2854 (-CH stretch), 1743 (-C=O stretch), 1597 (ring stretch), 1184, 1108 (-CH out of plane deformation in aromatic), 831 (aromatic - Cl).

^{1}H NMR δ (in ppm): 2.656 (3H, s); 6.481-6.512 (1H, d); 6.763-6.828 (2H, m); 7.596-7.955 (3H, m); 10.589 (1H, bs).

4-chloro-2-[(*E*)-(4-hydroxy-3-methylphenyl)diazenyl]-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (12). Yield 61% and m.p. 195^{0}C.

IR, ν cm^{-1}: 3401 (-OH stretch), 3081, 2923, 2853 (-CH stretch), 1725 (-C=O stretch), 1593 (ring stretch), 1186, 1100 (-CH out of plane deformation in aromatic), 830 (aromatic - Cl).

^{1}H NMR δ (in ppm): 2.38 (3H, s); 5.90 (1H, bs, OH); 6.52 (1H, d); 7.12 (2H, m); 7.34 (1H, m); 7.42 (1H, s); 8.08 (1H, d).

4-chloro-2-[(*E*)-(2,4-dihydroxyphenyl)diazenyl]-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (13). Yield 70% and m.p. 160^{0}C.

IR, ν cm^{-1}: 3434 (-OH), 2921, 2854 (-CH stretch), 1732 (-C=O stretch), 1507 (ring stretch), 1186, 1102 (-CH out of plane deformation in aromatic), 829 (aromatic - Cl).

^{1}H NMR δ (in ppm): 5.90-6.20 (2H, bs); 6.49 (1H, d); 6.52 (1H, d); 6.60 (1H, m); 7.42 (1H, s); 7.32 (1H, d); 8.08 (1H, d).

5-[(*E*)-(4-chloro-8-oxo-8*H*-chromeno[8,7-*d*][1,3]thiazol-2-yl)diazenyl]-2-hydroxy benzaldehyde (14). Yield 52% and m.p. does not melt upto 250^{0}C.

IR, ν cm^{-1}: 3425 (-OH stretch), 3084, 3069, 2918, 2850 (-CH stretch), 1738 (-C=O stretch), 1585 (ring stretch), 1186, 1108 (-CH out of plane deformation in aromatic), 816 (aromatic - Cl).

^{1}H NMR δ (in ppm): 5.91 (1H, bs, OH); 6.54 (1H, d); 7.40 (1H, s); 7.50 (1H, m); 8.10 (1H, d); 8.20 (1H, m); 8.27 (1H, d); 9.81 (1H, s).

5-chloro-3-[(*E*)-(4-chloro-8-oxo-8*H*-chromeno[8,7-*d*][1,3]thiazol-2-yl)diazenyl]-2-hydroxybenzaldehyde (15). Yield 65% and m.p. 210^{0}C.

IR, ν cm^{-1}: 3436 (-OH stretch), 3070, 3047, 2927 (-CH stretch), 1739, 1681 (-C=O stretch), 1568 (ring stretch), 1171, 1114 (-CH out of plane deformation in aromatic), 830 (aromatic - Cl).

^{1}H NMR δ (in ppm): 5.85 (1H, bs, OH); 6.48 (1H, d); 7.40 (1H, s); 8.05 (1H, s); 8.14 (1H, d); 8.35 (1H, s); 9.90 (1H, s).

2-[(*E*)-(5-amino-2-hydroxyphenyl)diazenyl]-4-chloro-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (16). Yield 58% and m.p. 188^{0}C.

IR, ν cm^{-1}: 3350, 3206 (-NH stretch), 1731 (-C=O stretch), 1631, 1581 (ring stretch), 1118 (-CH out of plane deformation in aromatic), 830 (aromatic - Cl).

^{1}H NMR δ (in ppm): 4.80 (2H, bs); 5.78 (1H, bs, OH); 6.48-6.52 (3H, m); 6.98 (1H, d); 7.42 (1H, s); 8.07 (1H, d).

3-[(*E*)-(4-chloro-8-oxo-8*H*-chromeno[8,7-*d*][1,3]thiazol-2-yl)diazenyl]-2-hydroxy-5-nitro benzaldehyde (17). Yield 60% and m.p. 235^{0}C.

IR, ν cm^{-1}: 3444 (-OH stretch), 3070, 2923, 2885 (-CH stretch), 1735 (-C=O stretch), 1578 (ring stretch), 1182, 1095 (-CH out of plane deformation in aromatic), 822 (aromatic - Cl).

^{1}H NMR δ (in ppm): 6.30 (1H, bs, OH); 6.48 (1H, d); 7.48 (1H, s); 8.02 (1H, d); 8.45 (1H, s); 8.80 (1H, s); 10.02 (1H, s).

2-[(*E*)-(4-aminophenyl)diazenyl]-4-chloro-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (18). Yield 64% and m.p. 168^{0}C.

IR, ν cm^{-1}: 3340, 3370 (-NH stretch), 3201, 3070, 2923 (-CH stretch), 1736 (-C=O stretch), 1587 (ring stretch), 1187, 1109 (-CH out of plane deformation in aromatic), 830 (aromatic - Cl).

^{1}H NMR δ (in ppm): 5.72 (2H, bs, NH_2); 6.60 (1H, d); 7.45 (2H, t); 7.51 (1H, s); 7.86 (2H, t); 8.09 (1H, d).

4-chloro-2-{(*E*)-[4-(methylamino)phenyl]diazenyl}-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (19). Yield 61% and m.p. 215^{0}C.

IR, ν cm^{-1}: 3445 (-NH stretch), 1750 (-C=O stretch), 1596 (ring stretch), 1114, 1104 (-CH out of plane deformation in aromatic), 909 (aromatic - Cl).

^{1}H NMR δ (in ppm): 3.00 (3H, s); 5.61 (1H, bs); 6.75 (1H, d); 7.15 (1H, d); 7.50 (2H, t); 7.95 (2H, t); 8.21 (1H, d).

4-chloro-2-{(*E*)-[4-(dimethylamino)phenyl]diazenyl}-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (20). Yield 69% and m.p. 205^{0}C.

IR, ν cm^{-1}: 3435 (-NH stretch), 3065, 2921, 2853 (-CH stretch), 1740 (-C=O stretch), 1599 (ring stretch), 1147, 1117 (-CH out of plane deformation in aromatic), 826 (aromatic - Cl).

^{1}H NMR δ (in ppm): 2.40 (6H, s); 6.72 (1H, d); 7.13 (1H, d); 7.48 (2H, t); 7.91 (2H, t); 8.24 (1H, d).

2-[(*E*)-(2-amino-5-chlorophenyl)diazenyl]-4-chloro-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (21). Yield 52% and m.p. 245^{0}C.

IR, ν cm^{-1}: 3451 (-NH stretch), 3077, 2925 (-CH stretch), 1737 (-C=O stretch), 1577 (ring stretch), 1185, 1107 (-CH out of plane deformation in aromatic), 825 (aromatic - Cl).

^{1}H NMR δ (in ppm): 5.74 (2H, bs, NH_2); 6.57 (1H, d); 7.12 (1H, d); 7.50 (1H, s); 7.78 (2H, m); 8.07 (1H, d).

2-[(*E*)-(4-amino-2-nitrophenyl)diazenyl]-4-chloro-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (22). Yield 60% and m.p. 185^{0}C.

IR, ν cm^{-1}: 3444 (-NH stretch), 3081, 2925, 2854 (-CH stretch), 1737 (-C=O stretch), 1579 (ring stretch), 1186, 1110 (-CH out of plane deformation in aromatic), 831 (aromatic - Cl).

^{1}H NMR δ (in ppm): 5.96 (2H, bs, NH_2); 6.57 (1H, d); 7.34 (1H, d); 7.50 (1H, s); 7.78-7.91 (2H, m); 8.01 (1H, d).

2-[(*E*)-(4-amino-3-nitrophenyl)diazenyl]-4-chloro-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (23). Yield 74% and m.p. 165^{0}C.

IR, ν cm^{-1}: 3448 (-NH stretch), 3084, 2923, 2850 (-CH stretch), 1738 (-C=O stretch), 1585 (ring stretch), 1187, 1112 (-CH out of plane deformation in aromatic), 817 (aromatic - Cl).

^{1}H NMR δ (in ppm): 6.30 (2H, bs, NH_2); 6.60 (1H, d); 7.40 (1H, d); 7.50 (1H, s); 7.84-7.92 (2H, m); 8.10 (1H, d).

2-[(*E*)-(2-amino-5-methylphenyl)diazenyl]-4-chloro-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (24). Yield 56% and m.p. 235^{0}C.

IR, ν cm^{-1}: 3443 (-NH stretch), 3076 (-CH stretch), 1736 (-C=O stretch), 1577 (ring stretch), 1185, 1108 (-CH out of plane deformation in aromatic), 826 (aromatic - Cl).

^{1}H NMR δ (in ppm): 2.11 (3H, s); 5.70 (2H, bs, NH_2); 6.58 (1H, d); 7.04 (1H, d); 7.50 (1H, s); 7.60 (2H, m); 8.07 (1H, d).

2-[(*E*)-(4-amino-3-methylphenyl)diazenyl]-4-chloro-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (25). Yield 69% and m.p. 219^{0}C.

IR, ν cm^{-1}: 3451 (-NH stretch), 3077 (-CH stretch), 1736 (-C=O stretch), 1577 (ring stretch), 1185, 1107 (-CH out of plane deformation in aromatic), 824 (aromatic - Cl).

^{1}H NMR δ (in ppm): 2.16 (3H, s); 5.64 (2H, bs, NH_2); 6.58 (1H, d); 7.21 (1H, d); 7.34-7.39 (2H, m); 7.50 (1H, s); 8.07 (1H, d).

2-[(*E*)-(2-amino-5-bromophenyl)diazenyl]-4-chloro-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (26). Yield 81% and m.p. 194^{0}C.

IR, ν cm^{-1}: 3443 (-NH stretch), 3077, 2924 (-CH stretch), 1737 (-C=O stretch), 1577 (ring stretch), 1185, 1106 (-CH out of plane deformation in aromatic), 824 (aromatic - Cl).

^{1}H NMR δ (in ppm): 5.70 (2H, bs, NH_2); 6.60 (1H, d); 7.09 (1H, d); 7.49 (1H, s); 7.70 (2H, m); 8.07 (1H, d).

2-[(*E*)-(2-amino-5-methoxyphenyl)diazenyl]-4-chloro-8*H*-chromeno[8,7-*d*][1,3]thiazol-8-one (27). Yield 74% and m.p. 221^{0}C.

IR, ν cm^{-1}: 3384 (-NH stretch), 3078, 2926 (-CH stretch), 1736 (-C=O stretch), 1579 (ring stretch), 1185, 1108 (-CH out of plane deformation in aromatic), 829 (aromatic - Cl).

^{1}H NMR δ (in ppm): 3.81 (3H, s); 5.68 (2H, bs, NH_2); 6.58(1H, d); 7.14 (1H, d); 7.54 (1H, s); 7.74 (2H, m); 8.06 (1H, d).

BIOLOGICAL STUDIES:

Some derivatives of amino coumarins shows anti microbial activities such as 2-amino benzopyranothiazoles and pyrazoles. Hence in the present work, we synthesized these compounds and checked for their antimicrobial activities.

The antimicrobial activity of these compounds can be studied by paper disc diffusion method. The paper disc is impregnated with desired compounds; usually 1% of the solution is prepared. The standard Wattmans filter paper disc is dipped in the solution and placed on the medium with the test organisms preferably one gram positive and one gram negative, so that the antibacterial spectrum of the given compound can be found out. The plates are incubated for 24 hours and zone of inhibition, if any is observed and recorded. The compound diffuses in the medium and inhibits the test organism on the medium producing a visual zone of inhibition.

Sr. No.	test organism	Compound									
		8	9	10	11	12	13	14	15	16	17
01	*S. aureus.*	-	+	+	-	-	+	-	+	+	+
02	*S. typhi.*	-	+	-	+	-	-	+	-	-	+

Table 01: Biological study of azo compound of phenols and 2-amino-4-chloro-8H-chromeno[8,7-d](1,3)-thiazol-8-one.
Key : + zone of inhibition observed; - zone of inhibition not observed.

Sr. No	test organism	Compound									
		18	19	20	21	22	23	24	25	26	27
01	*S. aureus.*	-	-	+	+	-	+	+	-	+	-
02	*S. typhi.*	-	-	-	-	-	-	+	-	-	-

Table 02: Biological study of azo compound of anilines and 2-amino-4-chloro-8H-chromeno[8,7-d](1,3)-thiazol-8-one.
Key : + zone of inhibition observed; - zone of inhibition not observed.

The compounds **9, 10, 13, 15, 16, 17, 20, 21, 23, 24** and **26** were found to be effective against the given test organism *S. aureus*, whereas compound **9, 11, 14, 17** and **26** were found to be effective against the given test organism *S. typhi*. Of these compounds **9, 17** and **26** was found to be the most effective.

RESULT AND DISCUSSION:

Salicylaldehyde (**1**) was chlorinated by using sulphuryl chloride give compound **2**. The compound **2** was nitrated by using fuming nitric acid and acetic anhydride gives compound 3. Compound **3** was heated with sodium acetate and acetic anhydride at 175^0C for about 8 hrs forming compound **4** which was reduced further by using calcium chloride and zinc powder gives compound **5** (8-amino-6-chlorocoumarin). The 8-amino-6-chloro coumarin was with 95% acetic acid and potassium thiocyanate followed by the reaction with liquid bromine in 20 ml of acetic acid. Finally the product was obtained by the neutralization with liquid ammonia. The solid obtained was yellow coloured 2-amino benzopyranothiazole **6**.

The 2-amino benzopyranothiazole **6** can be diazotized and then treated with various aromatic phenols and anilines forming series of diazo compounds with moderate yield **8-27**. The structure of diazo compound can be confirmed from its IR and NMR spectra. The coumarin protons show the signals at nearly 6.40-6.60, 7.35-7.45 and 8.0-8.1 in NMR spectra of both diazo-compounds of it with phenols and anilines.

The compounds are then tested for their antimicrobial activity, some of them are effective (**9, 17** and **26** are more effective) against the given test organism *S. aureus* and *S. typhi*.

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