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Green approach for the synthesis of novel acid red 37 derivatives, their evaluation as antimicrobial

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KEYWORDS

Acid red 37;
Schiff bases;
antimicrobial.

A B S T R A C T

Acid red 37 reacted with p-chlorobenzaldehyde, p-methoxybenzaldehyde, anthrone to afford new compounds (1-3) via condensation with the amino and methyl group. p-Nitrobenzaldehyde, anthraldehyde gave compounds (4-5) from condensation with the amino and addition with the imide –NH, whereas p-N, N-dimethylamino benzaldehyde yielded compound (6) through condensation with the amino, methyl and addition of the imide -NH. The formation of the new compounds were done in dry media under the free-solvent condition by fusion. Some trials to study the reaction under reflux in alcohol and /or acetonitrile up 30 hrs were failed. This type of excellent method avoids use of hazardous solvents, larger reaction time and tedious work up procedure. The advantage of this method is the excellent yield. Compounds (7-9) with heterocyclic ring; hydrazone compounds (10-11) and compound (12) respectively, were afforded via the reaction of the compounds (1-6) with hydrazine hydrate. Elucidation of the structures based on elemental analyses, IR, ^{1}HNMR& MS spectra. The antimicrobial activity of the new compounds were screened

Introduction

Schiff bases form an interested and important group of compounds, possess excellent application in many fields. Such as biological, inorganic and analytical chemistry (Cimerman et al., 2000; Singh et al., 1975; Perry et al., 1988; Elmali et al., 2000; Patel et al., 1999) and wide use in the industry and their interesting pharmacological activity as antibacterial (Sari et al., 2003; Karia F.D. and Parsania, 1999; More et al., 2001), antifungal (Singh and Dash 1988; Rajendra and Karvembu, 2002 Calis et al., 2002), antimicrobial (Padeya et al., 1999;] Sheikh et al., 2001;

Deshmukh. and Doshi 1995), anticonvulsant (Sridhar et al., 2003), anti HIV (Sridhar et al., 2002), anti-inflammatory and antitumor (Lin et al., 2006; Elinos-Baez et al., 2005). A series of Schiff bases have been synthesized from the condensation of (4.4'-diaminodiphenylsulphone) with various aromatic or heterocyclic aldehydes and the new compounds were evaluated for their *in vitro* activity against several microbes (Wadher et al., 2009).

Schiff base derivatives of 4-methylpyridin-2-amine have been screened for their antimicrobial activities (Vora et al., 2009). Some Schiff bases of [4-(amino)-5-phenyl-4H-1, 2, 4-triazole-3-thiol were screened for their antianxietic activity (Jubie et al., 2011) Schiff bases derived from 2-amino 4,6- dimethyl benzothiazole and pyridine/pyrrole 2-carboxyaldehyde and their complexes were also screened for the antimicrobial activity, antibacterial activity against bacteria like s-aureus, E-coli and antifungal activity against A-Niger and A-Flavus (Kulkarni et al., 2012).

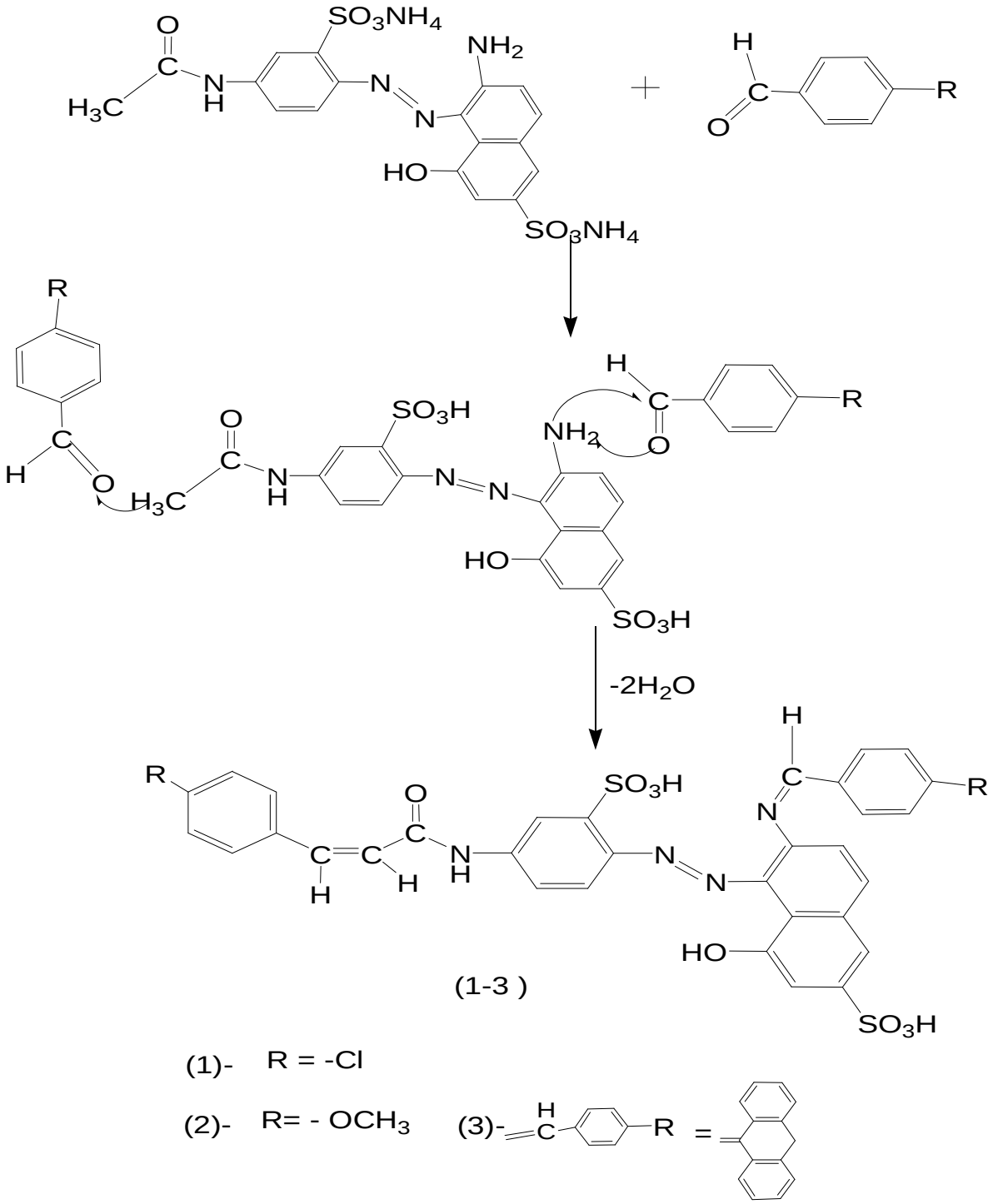
Mild and significant Schiff bases have been synthesized from different aldehyde and diamine using P_2O_5/SiO_2 as catalyst by crushing in a mortar at room temperature under free solvent conditions (Devidass et al., 2011). Primary aromatic amines reacted with aryl aldehydes catalyzed by lemon juice as natural acid under solvent-free conditions and gave Schiff bases in good yields (Patil et al., 2012).This work deals with the preparation of novel compounds via condensation reaction of some aldehydes and ketones with acid red 37 and their evaluation as antimicrobial .

Result and Discussion

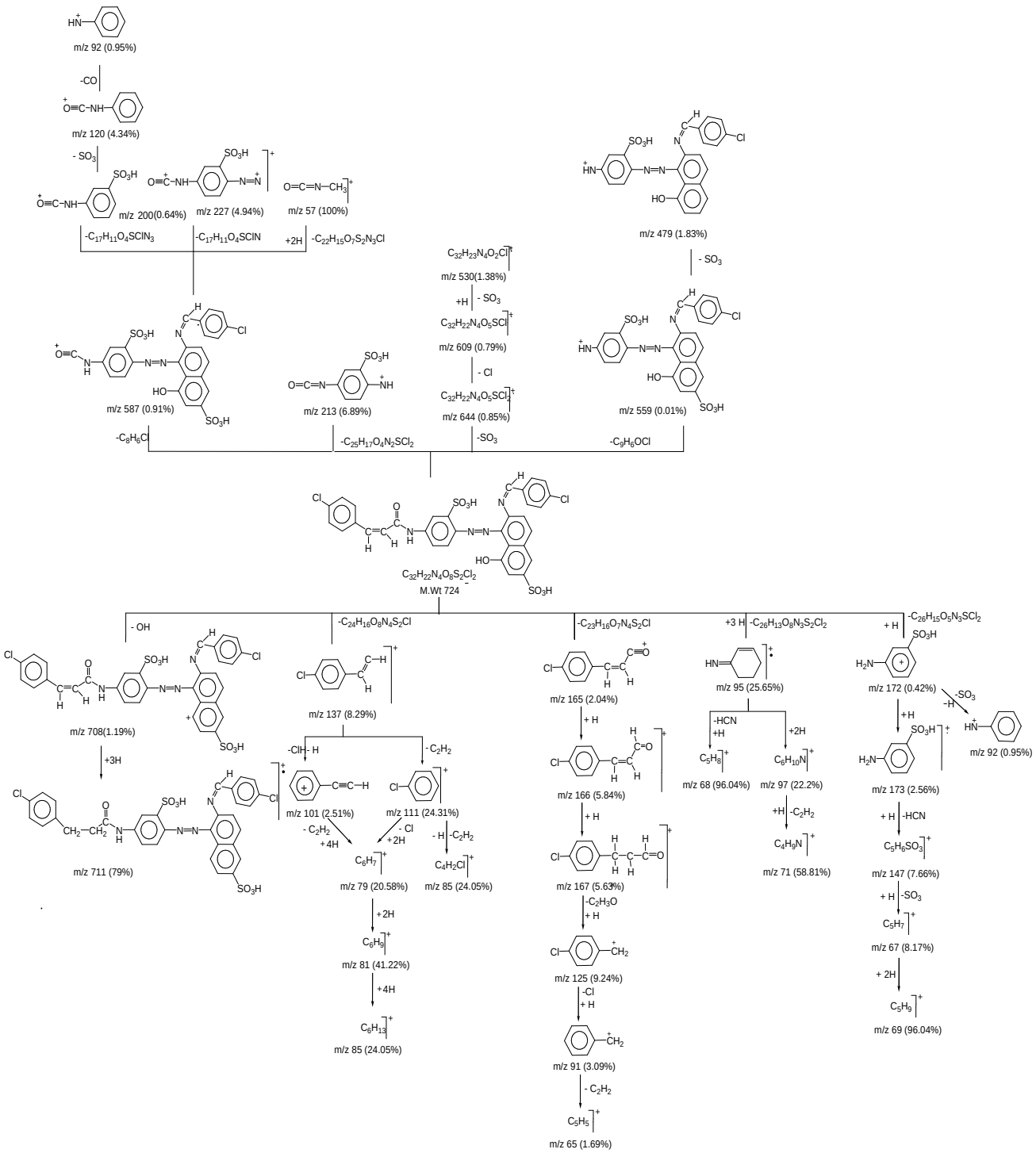
Acid red 37 reacted with some aromatic aldehydes such as p-chlorobenzaldehyde, p-methoxybenzaldehyde, p-N, N-dimethylamino benzaldehyde, p-nitrobenzaldehyde, anthraldehyde & anthrone. The reactions in alcohol and /or acetonitrile under reflux failed to give Schiff bases. The new compounds (1), (2), (3), (4), (5)& (6) were obtained by fusion.

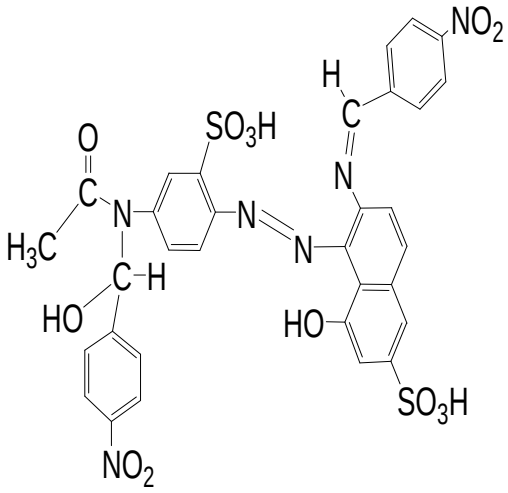
The structures were confirmed according to their elemental analysis, IR, ^{1}HNMR, MS and chemical reaction. The IR spectra for (1), (2), (3) showed the absence of ν_{NH2} at 3439- 3345 cm^{-1}, shift of $\nu_{C=O}$ with respect to the parent compound which can be attributed to the formation of the conjugated system -C=C-CO –N- at 1699 cm^{-1}, 1683 cm^{-1}, 1661 cm^{-1} respectively, and the appearance of $\nu_{C=N}$ at 1591cm^{-1}, 1604 cm^{-1}, 1589 cm^{-1} respectively. Quantitative determination of acid groups indicated the presence of two sulphonic groups. The ^{1}HNMR spectra for compound (1) showed δ 10.21 ppm (1 H, NH proton), δ 8.12-7.04 ppm(17 H, aromatic and alkene protons), δ 5.37 ppm (1 H, OH proton), and δ 2.0 ppm (2 H,2SO_3 H protons). The MS spectra for compound (1) showed the molecular ion peak at m/z 724 (0.10%), the base peak at m/z 57 (100%) attributed to O=C=N-CH3 $^{\neg+\cdot}$. The fragmentations are schematically summarized in scheme (2) as follows. The MS spectrum for compounds (2) & (3) showed the molecular ion peak at m/z 716 (0.01%), m/z 831(0.01) and the base peak at m/z 79(100%) due to SO_3 $^{\neg+\cdot}$ & m/z 55 (100%) due to O=C=N-CH: $^{\neg+\cdot}$.

Scheme (1)



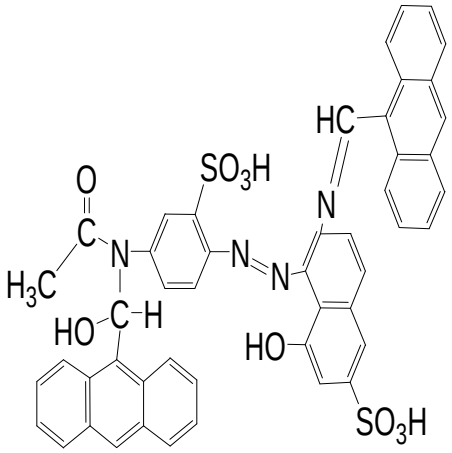
Scheme (2)


m/z 92 (0.95%)
-CO
m/z 120 (4.34%)
- SO3
m/z 200(0.64%)
m/z 227 (4.94%)
m/z 57 (100%)
-C17H11O4SClN3
-C17H11O4SCl
+2H
-C22H15O7S2N3Cl
m/z 479 (1.83%)
- SO3
C32H23N4O2Cl
m/z 530(1.38%)
+H
- SO3
C32H22N4O5SCl
m/z 609 (0.79%)
- Cl
C32H22N4O5SCl2
m/z 644 (0.85%)
m/z 587 (0.91%)
m/z 213 (6.89%)
m/z 559 (0.01%)
-C8H6Cl
-C25H17O4N2SCl2
-SO3
-C9H6OCl
C32H22N4O8S2Cl2
M.Wt 724
- OH
-C24H16O8N4S2Cl
-C23H16O7N4S2Cl
+3 H
-C26H13O8N3S2Cl2
+ H
-C26H15O5N3SCl2
m/z 708(1.19%)
m/z 137 (8.29%)
m/z 165 (2.04%)
m/z 95 (25.65%)
m/z 172 (0.42%)
-SO3
-H
m/z 92 (0.95%)
+3H
-Cl
- H
- C2H2
m/z 166 (5.84%)
-HCN
+H
+2H
m/z 173 (2.56%)
m/z 711 (79%)
m/z 101 (2.51%)
m/z 111 (24.31%)
- C2H2
+ 4H
- Cl
+ 2H
- H
-C2H2
m/z 167 (5.63%)
m/z 68 (96.04%)
m/z 97 (22.2%)
-HCN
m/z 147 (7.66%)
m/z 79 (20.58%)
m/z 85 (24.05%)
-C2H3O
m/z 125 (9.24%)
-SO3
m/z 67 (8.17%)
m/z 71 (58.81%)
m/z 81 (41.22%)
m/z 85 (24.05%)
m/z 91 (3.09%)
m/z 65 (1.69%)
m/z 69 (96.04%)

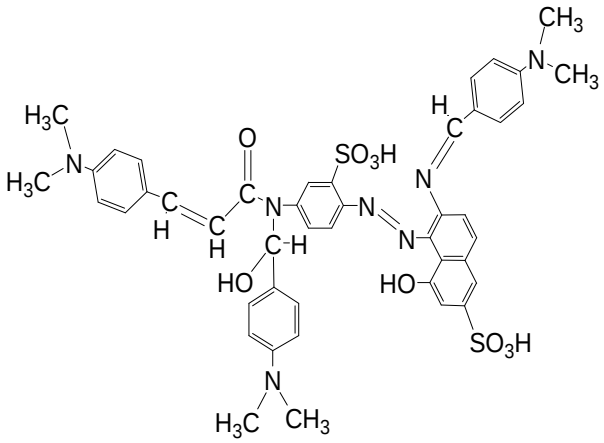


(4)

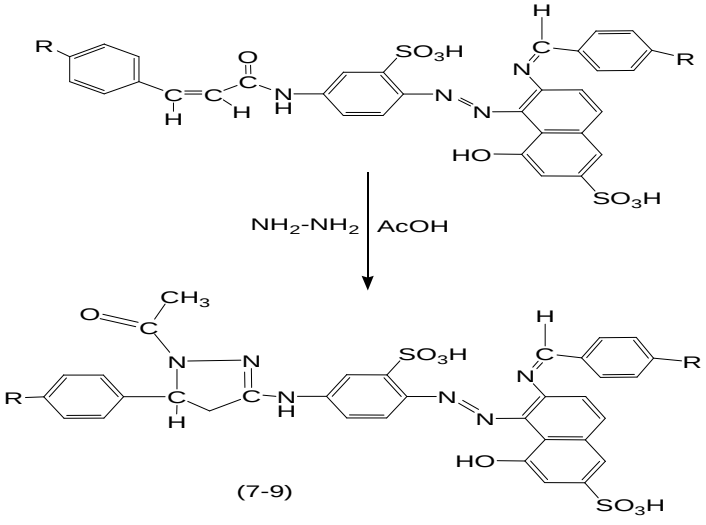
&



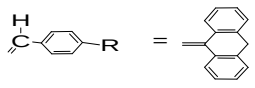
(5)

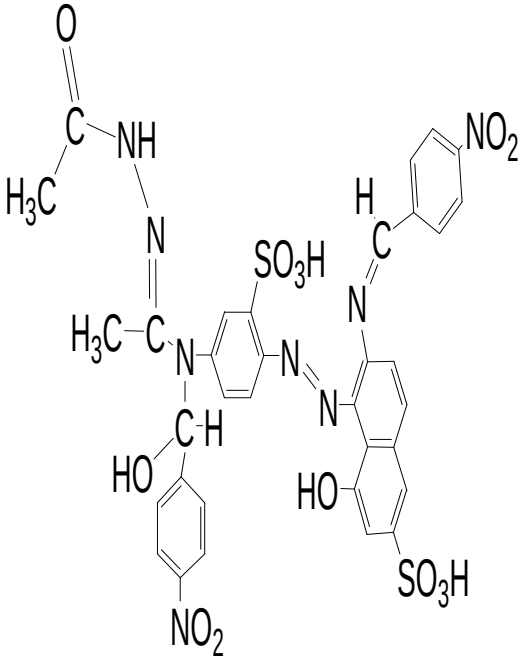


Scheme (3)



(7-9)

(7) R= -Cl
(8) R = OCH_3
(9) 



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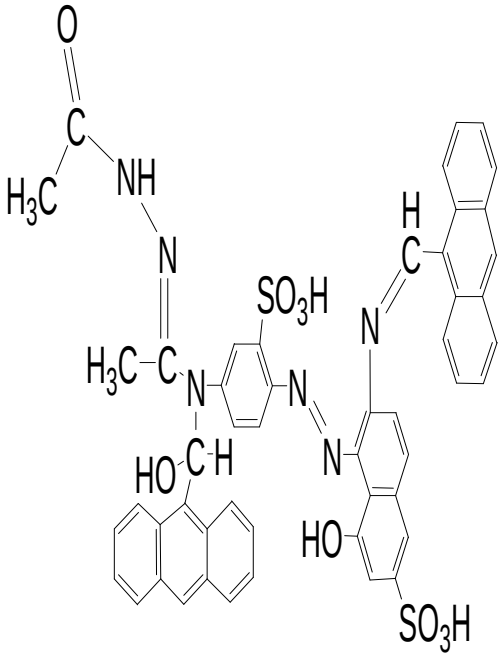
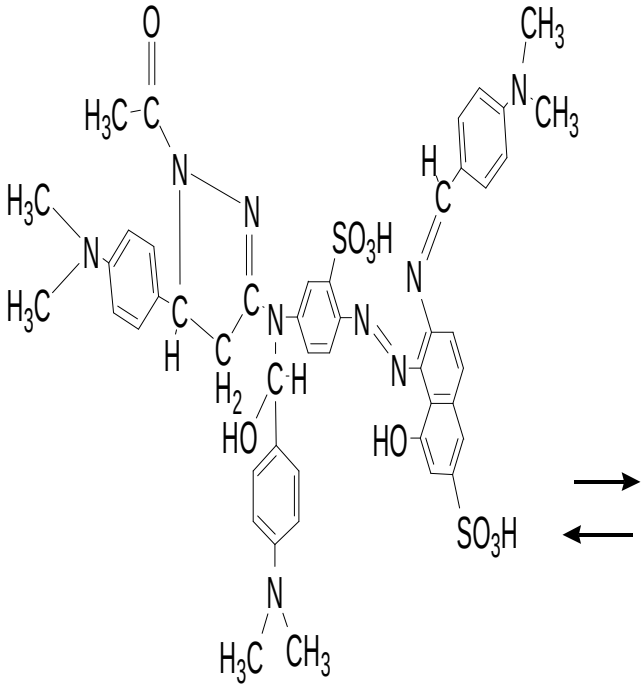
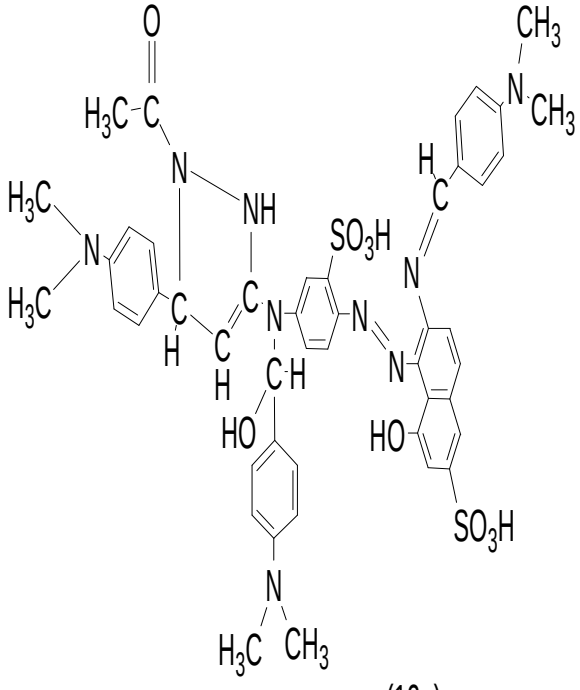


(10) (11)





(12) (12a)

Table.1 Antimicrobial activity of the products towards some types of bacteria

Sample	Inhibition zone diameter(mm/ mg sample)			
	***Escherichia Coli* (G^-)**	***Pseudomonas Aeruginosa* (G^-)**	***Staphylococcus aurous* (G^+)**	***Streptococcus faecalis* (G^+)**
Tetracycline	27	26	0.0	0.0
Amphotericin B	0.0	0.0	18	19
1	11	9	9	9
2	0.0	0.0	0.0	0.0
3	10	13	10	12
4	0.0	0.0	0.0	0.0
5	0.0	0.0	0.0	0.0
6	10	14	10	12

The reaction of Acid red 37 with p-nitrobenzaldehyde and anthraldehyde gave rise to new product (4) and (5).

IR, MS and elemental analysis confirmed their structures. The IR spectrum for Compound (4) showed 3441 (OH), 3342(NH),3040 (Ar C-H),3010 (alkene C-H),2900-2753 (C-H, aliph. Str.),1620 (C=N), 1669 (C=O), 1450 (C-H, aliph.bend.),1522,1349 (NO_2). The MS spectrum for compound (4) showed the molecular ion peak at m/z 764 (1.69%) and the base peak at m/z 150 (100%) can be attributed to p-O_2N-C_6 H_4 C≡O $^{\neg+}$; for compound (5) it showed M+2 $^{\neg+}$ at m/z 876 (0.39%) and the base peak at m/z 69 (100%) can be attributed to $CH_3CON{=}C{:}^{\neg+}$.

Product (6) obtained via the reaction of Acid red 37 with p-N,N-dimethylbenzaldehyde.

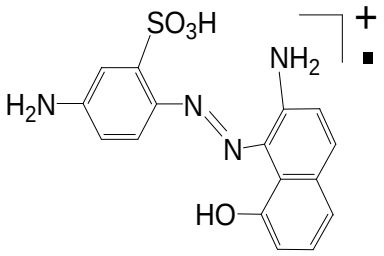
The structure was confirmed by elemental analysis, IR and MS spectra. The IR spectrum showed $\sqrt{}_{C=O}$ at 1664cm-^{1} due to the formation of the conjugated system -C=C-CO –N. The ^{1}HNMR spectrum for compound (6) showed δ 8.30-6.80 ppm (m,29H, Arom. proton), δ 5.39 ppm (s,1H,OH), δ 3.04 ppm (s,18 H, 3(-$N(CH_3)_2$), δ 2.08 ppm (s,2H, 2SO_3H). MS spectrum showed molecular ion peak M $^{\neg+}$ at 891 (6.51 %) and the base peak at m/z 55(100%) due to $C_4H_7^{\neg+}$ and /or $C_2HNO^{\neg+}$. Compounds (7- 9) formed via the reaction of compounds (1-3) with hydrazine hydrate via condensation, addition and finally cyclization reactions[25] cf. Scheme (3).

Elucidation of the structure based on elemental analysis, IR, ^{1}HNMR and mass spectra. The IR spectra showed $\nu_{C=O}$ shifted to 1662, 1674, 1669 respectively The ^{1}HNMR spectrum for compound (7) showed δ 10.2 ppm(1H for NH), δ 8.13 ppm(1H, for –N=CH-), δ 8-7 ppm(15H, arom-protons),δ 5.37 ppm (2H, for OH, CH), δ 2.49 ppm(3H, for $CH_3C{=}O$), δ 2.08 ppm(3H, for SO_3H,CH_2). The MS spectrum for compound (7) showed the molecular ion peak at m/z 782 (49.06%) M+1 $^{\neg+}$ and the base peak at m/z 60 (100%) due to Cl-CΞCH $^{\neg+}$.The MS spectrum for compound (8) showed the molecular ion peak at m/z 772(12.82), the base peak at m/z 69(100%), which can be attributed to CH3CO-N=C: $^{\neg+}$ .The MS spectrum for compound (9) showed M $^{\neg+}$ at 906 (8.24%) and the base peak at m/z

64(100 %) due to $C_5H_4^{\neg+}$.Compound (10) and (11) formed via condensation reaction of compounds(4) and (5) with hydrazine/AcOH.

Structures characterization based on elemental analysis, IR and MS spectra. The IR spectrum for compound (10) and (11) showed new absorption bands, two absorption bands at 3387 cm^{-1} due to ν_{NH}, two absorption bands at 1669 cm^{-1} and 1623 cm^{-1} for $\nu_{C=O}$ and $\nu_{N=C}$ respectively. The MS spectrum for compound (10) showed the molecular ion peak $M^{\neg+}$ at m/z 820 (2.96%) and the base peak at m/z 69(100%) attributed to $C_3H_4NO^{\neg+}$. The MS spectrum of compound (11) $M+2^{\neg+}$ at m/z 932(10.47%) and the base peak at m/z 80(100%) which can be attributed to $SO_3^{\neg+}$

New product (12) was obtained from the reaction of compound (6) with hydrazine hydrate/AcOH. The elemental analysis, IR , ^{1}HNMR and MS confirmed the structure. The IR spectrum showed new absorption band at 1650 cm^{-1} due to $\nu_{C=O.}$ The ^{1}HNMR showed δ 12.78 ppm (s, 1H for phenolic OH), δ 10.02 ppm (s,1H, for NH proton), δ 8.6 (s,1H for N=CH–Ar), δ 8.2-6.97 ppm(m, 19 H,aromatic protons), δ 6.91 ppm(s,1H,O-C-H), δ 6.8(d,1H, for –CH=C-N), δ 6.77 ppm(d,1H, Ar-CH-CH=C-N), δ 3.02 ppm(s,18 H,for 3(CH_3)$_3$), δ 2.08 ppm(s,3H for CH_3CO-N-) and δ 2.03ppm(s, 2H,for 2 SO_3H). The MS spectrum showed base peak at m/z 357(100%) can be attributed to



Biological activity

Measurement of Antimicrobial Activity using Diffusion disc Method: A filter paper sterilized disc saturated with measured quantity of the sample is placed on a plate containing solid bacterial medium (nutrient agar broth) or fungal medium (Doxs medium) which has been heavily seeded with the spore suspension of the tested organism.

After incubation, the diameter of the clear zone of inhibition surrounding the sample is taken as a measure of the inhibitory power of the sample against the particular test organism (Jawetz et al., 1974; Grayer Harbone, 1994; Muanza et al., 1994; Muanza et al., 1996; Irob et al., 1996). The antimicrobial activity of all compounds were tested and the results showed that compound (2, 4 &5) has no activity, while the compounds (1, 3 & 6) acquire moderate antimicrobial activity towards some types of bacteria cf. Table (1).

Experimental

Melting points were measured by a Gallen Kamp melting point apparatus. Thin layer chromatography was performed with fluorescent silica gel plates HF254 (Merck), and plates were viewed under UV light at 254 and 265 nm. The elemental analyses were determined by a Perkin-Elmer Analyzer 2440. Infrared spectra (√ cm^{-1}) were recorded on Bruker Vector Germany and on Mattson FT-IR 1000, using KBr disks. Mass spectra were measured on GCQ Finnigan MAT in Micro Analytical Center, Cairo University, Giza, Egypt. 1H-NMR spectra were recorded on Gemini 200 MHZ NMR spectrometer, in DMSO-d6 solution with TMS as internal standard in Micro Analytical Center, Cairo University, Giza, Egypt. The antibacterial

activity was determined in a laboratory belongs to the Micro- Analytical Center Cairo University.

The Preparation of compounds (1-6). General procedure for the preparation of compounds (1-6) by fusion:

A mixture of the aldehyde (1mmol) and Acid red 37 (1mmol) were fused (under free solvent) condition, the new compound obtained was crystallized from the suitable solvent.

Compound (1) 6-(-4-chlorobenzylidene amino)-5-(4-(3-(4-chlorophenyl) acryl amido) -2-sulphophenyl) diazenyl)-4-hydroxynaphthalene-2-sulphonic acid

Brown crystals, crystallized from ethanol, yield: 64.80 % ; m.p. 200^{o}C, I.R. cm^{-1} (√): 3441(OH), 3338(NH), 3090(Ar C-H), 3040 (alkene C-H), 2986-2841 (C-H, aliph. Str.), 1699(C=O), 1620 (C=N),. 1399 (C-H, aliph.bend.). . MS spectrum m/z(%): 726(1.10) M+1^{+}, the base peak at 57(100) CH_3-N=C=O $^{+}$. The ^{1}HNMR showed δ 10.25 ppm (s,1H, for NH proton), δ 8.22 ppm(s,1H, for N=CH-Ar), δ 8 - 7.05 ppm(m, 15 H for aromatic protons), δ 8.1 ppm(s,1 H for C=CH-CO), δ 7.04 ppm(s,1H forArCH=), δ 6.08 ppm(s,1H for=CH-CO), δ 5.37 ppm (s, 1H for phenolic OH),), and δ 2.08 ppm (s,2H, for 2SO_3H). Anal. calcd. for $C_{32}H_{22}N_4S_2O_8Cl_2$ (725): C, 52.96; H, 3.03; N, 7.72; S, 8.82; Cl, 9.72. Found: C, 52.75; H, 3.00; N, 7.66; S, 8.77; Cl, 9.67.

Compound (2)6-(-4-methoxy benzyl ideneamino) -5- (4-(3-(4-methoxyphenyl) acrylamido)-2- sulphophenyl) diazenyl) – 4-hydroxynaphthalene- 2-sulphonic acid

Brown crystals, crystallized from ethanol, yield: 65.40% ; m.p 290^{o}C.I.R. cm^{-1} (√): 3600- (OH), 3328(NH),3069 (Ar C-H),3004 (alkene C-H),2936-2836 (C-H, aliph. Str.), 1683 (C=O), 1623(C=N),. 1463 (C-H, aliph.bend.) , 1254 (assymmetric C-O-C), 1030(symmetric C-O-C) .The MS spectrum m/z(%): 716 (0.10) M $^{+}$, base peak at 81 (100%) which can be attributed to SO_3H^{+}. Anal. calcd. for $C_{34}H_{30}N_4O_{11}S_2$ (716): C,56.98; H, 3.91; N,7.82; S, 8.93. Found: C, 56.85; H,3.7 5; N, 7.80; S ,8.80.

Compound (3) 5-((4-(2-(anthracen-10 (9*H*)- ylidene(acetamido)-2-sulphophenyl) diazenyl) -6- (anthracen-10 (9*H*) -ylidene amino)-4-hydroxynaphthalene-2-sulphonic acid

Black crystals, crystallized from ethanol, yield: 63.44 % ; m.p 240^{o}C. I.R. cm^{-1} (√): 3416 (OH),3200 (NH), 3040 (Ar C-H),3010 (alkene C-H), 2900-2800 (C-H, aliph. Str.), 1661(C=O), 1623(C=N), ,1472 (C-H, aliph.bend.). ^{1}HNMR showed δ 10.25 ppm (s,1H, for NH proton), δ 8.2 ppm(s,1 H for C=CH-CO), δ 8.10 - 7.05 ppm(m, 23 for aromatic protons), δ 5.42 ppm (s, 1H for phenolic OH), δ 3.8 ppm(s, 4H, for 2 CH_2), and δ 2.03 ppm (s,2H, for 2SO_3H). MS spectrum m/z (%): 832(0.17) M $^{+}$, 775(1.64), 55(100)which can be attributed to $C_4H_7^{+}$. Anal. calcd. for $C_{46}H_{34}N_4S_2O_9$ (832): C,66.34; H, 5.06; N,6.73; S, 7.69. Found: C,66.00; H,5.00; N, 6.65; S, 7.55.

Compound (4) (4-(N-(hydroxyl(4-nitro phenyl) methyl)acetamido-2-sulpho phenyl)diazenyl)-6-4-nitrobenzylidene amino)-4-hydroxynaphthalene-2-sulphonic acid

Brown crystals, crystallized from ethanol , yield: 65 %; m.p 185^{o}C. I.R. cm^{-1} (√): 3441 (OH), 3342(NH),3040 (Ar C-H),3010 (alkene C-H),2900-2753 (C-H, aliph. Str.), 1669 (C=O), 1620 (C=N), 1450 (C-H, aliph.bend.),1522,1349 (NO_2). ^{1}HNMR showed δ 10.27 ppm (s,1H, for

NH proton), δ 8.64 ppm(s,1 H for N=CH-Ar), δ 8.43- 7.01 ppm(m, 15 H, for aromatic protons), δ 6.20 ppm(s,1H,for N-CH(-O-)-Ar), δ 5.79 ppm(s,1H for N-C(OH)-Ar), δ 5.43 ppm (s, 1H for phenolic OH),), and δ 2.08 ppm (s,2H, for $2SO_3H$). MS spectrum m/z(%): 764(1.69) $M^{+\cdot}$, base peak 150(100)which can be attributed to $HN{=}CH\text{-}C_6H_4\ NO_2^{+\cdot}$.Anal. calcd. for $C_{32}H_{24}N_6\ S_2O_{13}$ (764): C,50.26; H, 3.14; N,10.99; S, 8.37. Found: C,49.85; H, 3.00; N,10.86; S, 8.25.

Compound (5) 5-((4-(N-(anthracen-10-yl(hydroxyl)methyl) acetamido)-2-sulpho phenyl)diazenyl)-6-(anthracen-10-yl-methylenamino)-4-hydroxynaphthalene-2-sulphonic acid

Yellowish brown crystals crystallized from ethanol yield: 63.25 %; m.p 270°C. I.R. cm^{-1} (√): 3400 (OH), 3390 (NH),3040 (Ar C-H), 3010 (alkene C-H), 2950-2800 (C-H, aliph. Str.), 1667(C=O), 1624 (C=N), 1478(C-H, aliph.bend.). MS spectrum m/z(%): 876 (0.39) $M{+}2^{+\cdot}$, 69(100%)which can be attributed to $CH_3CON{=}C\text{:}^{+\cdot}$. Anal. calcd. for $C_{48}H_{34}N_4\ S_2O_9$ (874): C,65.90; H,3.89; N,6.40; S, 7.35. Found: C,65.75; H,3.80; N, 6.35; S, 7.25.

Compound (6) 5-(4-((3-(4-(dimethy amino)phenyl)-N-((4- (dimethy amino) phenyl) (hydroxyl) methyl) acrylamido)-2-sulphophenyl)diazenyl)-6-((4--(dimethyl amino) benzylideneamino)-4-hydroxynaphthalene-2-sulphonic acid

Purple crystals, crystallized from ethanol. Yield: 32.45 %; m.p 260°C.

I.R. cm^{-1} (√): 3445 (OH),3347 (NH),3050 (Ar C-H),3010 (alkene C-H),2906-2820 (C-H, aliph. Str.), 1664(C=O), 1597 (C=N), 1467(C-H, aliph.bend.). ^{1}HNMR showed δ 9.67-7.05 ppm(19 H, aromatic protons), δ 8.18 ppm(s,1H for N=CH-Ar), δ 6.80 ppm(s,1H for Ar CH=), δ 6.77 ppm(s,1H for =CH-CO-), δ 5.37 ppm (1 H, OH proton), δ 3.04 ppm (s,18H for 3 $N(CH_3)_2$) and δ 2.0 ppm (2 H, $2SO_3$ H protons). MS spectrum m/z(%): 889 (6.50) $M{-}2^{+}$, 55(100) due to $C_4H_7^{+}$ Anal. Calcd. for $C_{45}H_{45}N_7\ S_2O_9$ (891): C, 60.60; H, 5.05; N,10.99; S,7.18. Found: C,60.54; H, 4.99; N, 10.87; S, 7.08.

General procedure for the preparation of compounds (7-12)

A mixture of (1 mmole) of compound (1red) and (1 mmole) of hydrazine hydrate in 20 ml acetic acid was refluxed for 2 h.

Compound (7) 5-((E)-(4-(1-acetyl-5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazol-3-ylamino)-2-sulfophenyl)diazenyl)-6-((Z)-4-chlorobenzylideneamino)-4-hydroxy naphthalene-2-sulfonic acid

Black-brown crystals, crystallized from ethanol, Yield: 70.45 %; It gave one spot on TLC., m.p·d. 320°C. I.R. cm^{-1} (√): 3405 (OH),3171 (NH),3050 (Ar C-H) , 2906-2820 (C-H, aliph. Str.), 1662(C=O), 1624, 1588 (C=N), 1475 (C-H, aliph.bend.). ^{1}HNMR showed δ 10.22 ppm (s,1H, for NH proton), δ 8.13 ppm(s,1 H for N=CH-Ar), δ 8.12- 7.04 ppm (m, 15 H, for aromatic protons), δ 6.93 ppm(s,1H,for ArCH(-N-)C), δ 5.43 ppm (s, 1H for phenolic OH), δ 1.90 ppm (2H for CH_2) and δ 2.08 ppm (s,2H, for $2SO_3H$). MS spectrum m/z(%):792(37.74) $M{+}2^{+\cdot}$, 60 (100) due to $CH_3COOH^{+\cdot}$. Anal. Calcd. for $C_{34}H_{26}N_6\ S_2O_8\ Cl_2$ (791): C, 51.58; H, 3.28; N,10.61; S,8.09. Found: C,51.45; H,3.25; N, 10.55; S, 8.00.

Compound (8) 5-(4-(1-acetyl-5-(4-methoxyphenyl)-4,5-dihydro-1*H*- pyrazol -3-ylamino) -2- sulpho phenyl) diazenyl)-6-(4-methoxybenzyl idene amino)-4-hydroxynaphthalene-2-sulphonic acid

Brown crystals crystallized from ethanol, Yield: 80 %; it gave one spot on TLC, m.p.d. 340°C. I.R. cm^{-1} (√):3398 (OH),3172 (NH),3050 (Ar C-H) , 2906-2820 (C-H, aliph. Str.), 1716, 1674 (C=O), 1623, 1588 (C=N), 1476 (C-H, aliph.bend.). MS spectrum m/z(%): 772(12.82) $M^{+\cdot}$, 69(100) due to $CH_3CON{=}C{:}^{+}$. Anal. Calcd. for $C_{36}H_{32}N_6S_2O_{10}$ ~(772): C, 55.95; H, 4.14; N, 10.88; S, 8.29. Found: C,55.58; H,4.00; N, 10.77; S, 8.11.

Compound (9) pyrazole derivative of compound (3)

Black crystals crystallized from ethanol, Yield: 75.45 %; It gave one spot on TLC., m.p.d.at 280°C. I.R. cm^{-1} (√): 3405 (OH), 3173 (NH),3050 (Ar C-H) , 2906-2820 (C-H, aliph. Str.), 1677(C=O), 1623 (C=N), 1475 (C-H, aliph.bend.). MS spectrum m/z(%): 906 (8.24) $M^{+\cdot}$. The base peak at 64(100) due to $C_5H_4^{+}$. Anal. Calcd. for $C_{48}H_{36}N_6S_2O_8.H_2$ 0(906): C, 64.86; H, 4.05; N, 9.45; S, 7.20. Found: C, 64.78; H, 3.95; N, 9.33; S, 7.00.

Compound (10) Hydrazone derivative of compound (4)

Brown crystals crystallized from ethanol, Yield: 78.90 %; it gave one spot on TLC, m.p.d.at 300°C. I.R. cm^{-1} (√):3387 (OH), , 3309, 3171 (NH),3050 (Ar C-H), 2906-2820 (C-H, aliph. Str.), 1669(C=O), 1623 (C=N), 1476 (C-H, aliph.bend.) 1533, 1343 (NO_2). ^{1}HNMR showed δ 7.14 ppm(s,1H, for NH proton), δ 8.13 ppm (s,1 H for N=CH-Ar), δ 8.51- 7.04 ppm (m, 15 H, for aromatic protons), δ 6.93 ppm(s,1H,for ArCH(-N-)O), δ 5.43 ppm (s, 1H for phenolic OH), δ 2.49 ppm (s,3H, forCH_3), δ 2.08 ppm (s,2H, for $2SO_3H$)and δ 1.90 ppm (1H for HOCH(-N-)(Ar). MS spectrum m/z(%):818(11.15)M-2^{+}, The base peak at 69 (100) due to $CH_3CON{=}C{:}^{+\cdot}$. Anal. Calcd for.$C_{34}H_{28}N_8S_2O_{13}$ (820): C, 49.75; H, 3.41; N, 13.65; S, 7.80. Found: C,49.45; H, 3.33; N, 13.52; S, 7.45.

Compound (11)) Hydrazone derivative of compound(5)

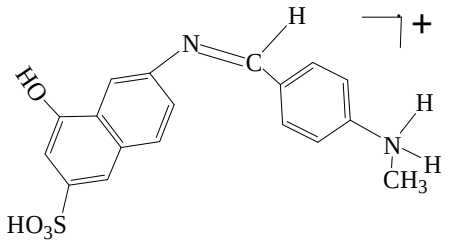
Black crystals crystallized from ethanol, Yield: 75.5 %; it gave one spot on TLC., m.p.d.at 260°C
I.R. cm^{-1} (√):3387 (OH),3305, 3175 (NH),3050 (Ar C-H) , 2906-2820 (C-H, aliph. Str.), 1669(C=O), 1623 (C=N), 1475 (C-H, aliph.bend.).MS spectrum m/z(%): 932 (10.47) $M^{+\cdot}$,the base peak at 81 (100) which can be attributed to SO_3H^{+}. Anal. Calcd. for $C_{50}H_{38}N_6S_2O_9$ (930): C, 64.51; H, 4.08; N, 9.03; S, 6.88. Found: C, 64.27; H, 3.95; N, 8.85; S, 6.75.

Compound (12) 6-(4- (dimethylamino) benzylideneamino)-4-hydroxy-5-(4-((1-acetyl-5-(4-(dimethylamino)phenyl)-4,5-dihydro-1*H*-pyrazol-3-yl)(4-(dimethyl amino) phenyl)(hydroxyl) methyl)amino) -2- sulphophenyl) diazenyl) naphthalene-2-sulphonic acid

Brown crystals crystallized from ethanol , Yield: 80 %; It gave one spot on TLC., m.p.d.at 300°C I.R. cm^{-1} (√):3416 (OH),3148 (NH),3050 (Ar C-H) , 2906-2820 (C-H, aliph. Str.), 1650(C=O), 1601 (C=N), 1433 (C-H, aliph.bend.).

^{1}HNMR showed δ 8.57ppm(s,1 H for N=CH-Ar), δ 8.23 – 6.88 ppm (m, 19 H, for aromatic protons), δ 6.77 ppm (s, 1H,

for N-CH-Ar), δ 5.10 ppm (s,1H, for phenolic OH proton), δ 4.93 ppm (s,1H, for methine proton), δ 3.03 ppm (s,18 H for $3N(CH_3)_2$), δ 2.08 ppm(s,3H for CH_3) δ 2.03 ppm(s, 3H for alcoholic OH,$2SO_3H$) and δ 1.99 , 1.90 ppm (s, forCH_2 protons).MS spectrum m/z(%): 947(6.30) $M^{\pm}$, the base peak 357(100%) attributed to



Anal. Calcd. for $C_{47}H_{49}N_9S_2O_9$ (947): C, 59.55; H, 5.14; N, 13.30; S, 6.75. Found: C, 58.98; H, 4.96; N,13.00; S, 6.55.

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