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Advances in Applied Science Research, 2011, 2 (1): 178-192

Pelagia Research Library
ISSN: 0976-8610
CODEN (USA): AASRFC

Synthesis, characterization, and biological activities of new 1-[(2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline derivatives

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ABSTRACT

*A new series of 1-[(2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline have been synthesized in 47 to 71% yield, by the reaction of N-cinnamoyl-N-2'-cyanoethyl-2,3-dichloroaniline with 2-[(N- cinnamoyl) 2,3-dichloroanilido] acetohydrazide. Pyrazolines are yellow, cream and brown color solids, having high melting points. Identity of these products has been established by elemental analysis and spectral data. Newly synthesized compounds (7a-t) have been tested for their antibacterial activity against gram positive bacteria S. albus , S. aureus and gram negative bacteria E. Coli and Pseudomonas poisonous .The compound (**7a, 7c, 7e, 7j, 7m, and 7s**) shown significant activity and the compound (7i, 7k, 7t,) have shown moderate activity. The same compounds were tested for their antifungal activity against Candida albicans, Aspergillus Niger and Alternaria alternata at concentration of 30 mg/mL using sabouraud dextrose agar media. The compound (**7b, 7j, 7m, and 7r**) shown significant activities and compound (7a, 7f, and 7g) were found to be moderately active against Candida albicans and Aspergillus Niger. All the other compounds did not show significant activity against the fungi at the concentration used. Some new compounds have been tested for antitubercular activity in-vitro using Mycobacterium tuberculosis. The compounds were incorporated into Lowenstein Jensen egg medium having concentrations of 10 and 100 mg/mL and were inoculated with Mycobacterium tuberculosis, $H_{27,}$ Rv strains, incubated at 37^0C and observed, the compound (**7a, 7c, 7e, 7j, and 7m**) inhibited the growth of Mycobacterium tuberculosis at 100mg/mL concentration other compounds were found to be inactive.*

Key words: 5-phenyl Pyrazoline, Synthesis, Characterization, and Biological Activities.

INTRODUCTION

Considerable attention has been focused on Pyrazolines and substituted Pyrazolines due to their interesting biological activities. They have found to possess anti-fungal[1], anti-depressant [2-7], anti-convulsant [8], anti-inflammatory [9-12], anti-bacterial [13-14], anti-cancer[15-16], anti-oxidant [17-18], anti-pyretic[19], anti-neoplastic activities [20-21], anti-viral [22], anti-amoebic [23-24], Acaricidal agro chemical fungicides or insecticides [25], anti-cholinergic [26-27], anti-diabetic [28], anti-HIV [29-32], anti-malarial [33], Anesthetic [34], Anaxiolytic [35], anti-parasitic[36], anti-allergic[37], anti-microbial [38-40], anti-tuberculosis[41-44],Tyrosinase inhibitor [45], Blue photo luminescence and electro luminescence [46], Food and chemical toxicology [47], Herbicidal [48-50], Hypoglycemic [51], Hypotensive [52], immuno suppressive [53], anti-tumor[54-55]. Moreover, many selectively chloro-substituted organic compounds show peculiar pharmacological and agrochemical properties. The work reported herein was aimed at the preparation of some new pyrazoline derivatives with anticipated biological activities.

MATERIALS AND METHODS

General

All chemicals were used of A.R. grade (either of B.D.H. or Excel-R or Extra pure E. Merck quality). The structures of the compounds were determined by elemental analysis, IR and NMR spectral data. All melting points were measured on an electro thermal melting point apparatus and are uncorrected. The infrared spectra were recorded in potassium bromide discs on a Pye Unicam SP 3-300 or a Shimadzu FT-IR 8101 PC infrared spectrophotometer. The ^{1}H –NMR (200 MHz) spectra were recorded in DMSO-d_6 on a Varian Mercury VX 200 NMR using TMS as the internal reference. Mass spectra were measured on a GCMS-QP 1000 EX spectrophotometer at 70 eV. Purity of the compounds is checked on T.L.C. using Silica Gel-G. Elemental analysis is performed on Carlo-Erba1108 analyzer

Synthesis of Ethyl-2-[2, 3-dichloroanilido] Ethanoate [1]:

A mixture of 2, 3-dichloroaniline (10ml) and diethylmalonate (20ml) was refluxed for forty five minutes in a round bottomed flask fitted with an air condenser of such a length (14") that ethanol formed escaped and diethylmalonate flowed back into the flask. Contents were cooled, ethanol (30 ml) was added, when malon-2,3dichlorodianilide separated out. It was filtered under suction. The filtrate was poured on to crushed ice (Ca160g) and stirred when ethyl-2-(2, 3-dichloroanilido) ethanoate precipitated as green mass. On recrystallization from aqueous ethanol (50%), ester was obtained as white crystals. Yield: 81%, M. P.: 88^{0}C, M. W.: 276. Anal. calculation for $C_{11}H_{11}N_1O_3Cl_2$: Found: C 47.7, H: 4.0, O: 17.2, N: 5.1, Cl: 25.4, Calcd. C: 47.8, H: 4.0, O: 17.4, N: 5.1, Cl: 25.7. *IR [KBr]* V_{max} Cm^{-1} : 1665-1660 [C=O diketone], 1290 [-O- Ester], 760-755 [2,3 disubstituted benzene], 1250 [C-Cl Stretching], 1590, 1520 , 1440 [C=C ring stretching], 3150 [N-H Stretching], 3040[C-H aromatic], 1330-1322 [C-H Stretching]. *PMR (DMSO):* δ 4.42 (2H, s, CO-CH_2-CO), 4.0 (2H, s, NH_2), 7.4-8.6 (3H, m, Ar-H), 9.2 (1H, s, CO-NH D_2O exchangeable), 10.6 [1H, s, Ar-NH D_2O exchangeable].

Synthesis of Ethyl-2-[(N-cinnamoyl) 2, 3- dichloroanilido] ethanoate [2]:

Cinnamoyl Chloride (10gm; 0.06 mol), dioxane (6 ml), Ethyl-2-(2,3-dichloroanilido) ethanoate (16.5 gm; 0.06 mol) and triethylamine (6.06 gm; 0.06 mol) were placed in a round bottomed

flask carrying reflux condenser having calcium chloride guard tube. The contents were heated on a boiling water bath for two hours and kept over night when triethylamine hydrochloride separated. It was filtered under suction and the filtrate was poured on to crushed ice (Ca180 g) and stirred when ethyl-2-[(N-cinnamoyl) 2, 3-dichloroanilido] ethanoate separated or solid. It was filtered under suction, dried and purified by recrystallization from aqueous methanol (1:1) in white crystals. Yield = 86 %, MP = 98°C Analytical calculation for $C_{20}H_{17}N_1O_4Cl_2$:[FW = 406], Calculated: N 3.4 , C 59.1, H 4.2 , O 15.8 , Cl 17.5 , Found : N 3.3, C 59.0 , H 4.1 , O 15.5 , Cl 17.4. *IR [KBr]* V_{max} cm^{-1}*:* 1740 [C=O diketone], 1330 [-C-O- Ester], 770[2,3- disubstituted benzene], 1080 [C-Cl Stretching], 1595, 1540 , 1470 [C=C Ring stretching], 3170 [N-H Stretching], 3050[C-H aromatic], 1340-1325 [C-H Stretching]. *PMR (DMSO):* δ 4.39 [2H, s, CO-CH_2-CO], 4.3 [2H, s, NH_2], 7.6-8.3 [3H, m, Ar-H], 9.6 [1H, s, CO-NH D_2O exchangeable], 10.2 [1H, s, Ar-NH D_2O exchangeable].

Synthesis of 2-[(N-cinnamoyl) 2, 3-dichloroanilido] acetohydrazide [3]:

Ethyl-2-[(N-cinnamoyl) 2, 3-dichloroanilido]ethanoate (12.2 gm; 0.03 mol), ethanol (8 ml) and hydrazine hydrate (15 ml; 80%) were mixed together and stirred for thirty five minutes. 2-[(N-cinnamoyl) 2, 3-dichloroanilido] acetohydrazide was filtered under suction and recrystallised from ethanol in white crystals. Yield; 73%, MP = 183°C, MW 392 Analytical calculation for $C_{18}H_{15}N_3O_3Cl_2$: Calculated: N 10.7 ,C 55.1 ,H 3.8 ,O 12.2, Cl 18.1, Found: N 10.6, C 55.0, H 03.7, O 12.1, Cl 18.0. *IR [KBr]* V_{max} cm^{-1}*:* 3180 [N-H Stretching], 3060 [C-H aromatic], 1690 [C=O diketone], 1445 [C-Cl aromatic], 1590, 1550, 1460 [C=C ring stretching]. *PMR (DMSO):* δ 4.48 (2H, s, CO-CH_2-CO), 4.5 (2H, s, NH_2), 7.4-8.1 (3H, m, Ar-H), 9.5 (1H, s, CO-NH D_2O exchangeable), 10.5 (1H, s, Ar-NH D_2O exchangeable).

Mono cyanoethylation of 2, 3-dichloroaniline [4]:

A 250 ml three necked flask equipped with a stirrer, reflux condenser and thermometer was charged with 2, 3-dichloro aniline (0.1mol, 16.2g), acrylonitrile (0.1mol, 10.6 g) and Cupric acetate monohydrate (1.02g, 4% by weight of the amine). The mixture was stirred and refluxed on boiling water bath for three hours. The dark mixture was then transferred to a 250 ml distilling flask fitted with a 15.2 cm modified vigorous column and the unchanged acrylonitrile was first collect at 100 mm (water pump). The distillation was continued and the unchanged 2, 3-dichloro aniline B.P. 252^{0}C/0.5mm was recovered. The N-Cyanoethyl-2, 3-dichloroaniline was obtained as light yellow colored viscous liquid at 175-176^{0}C/mm which solidified after keeping overnight. Yield: 15.7g (97%)., M.P. 82^{0}C

Preparation of Cinnamoyl Chloride [5]:

Cinnamic acid (10 g, 0.067mol) and thionyl Chloride (12.0 ml) were taken in a round bottomed flask fitted with a reflux condenser carrying a calcium chloride guard tube. The contents were refluxed on a water bath for two and half hours in a fume cupboard until the evolution of HCl gas ceased from the guard tube. After cooli

ng liquid was carefully transferred to a claisen flask and distilled under reduced pressure when unreacted thionyl chloride distilled over first. Cinnamoyl chloride was collected at 165-166^{0}C/ 18-20mm pressure.

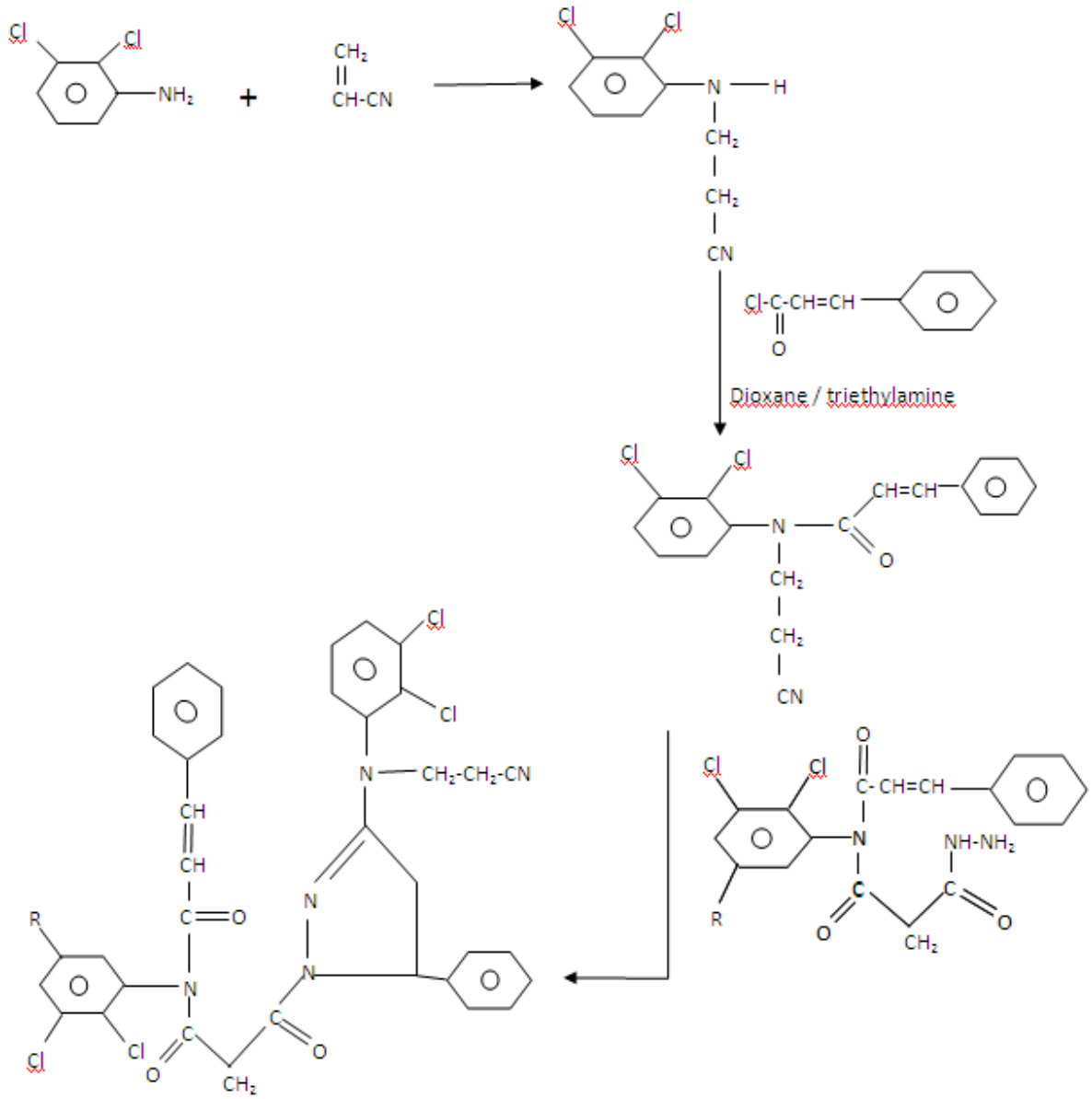
Synthesis of N-Cinnamoyl -N-2'-Cyanoethyl -2, 3-dichloroaniline [6]:

Solution of cinnamoyl chloride (3.5 g, 0.02 mol), dioxane (2ml), N-2'-cyanoethyl -2, 3-dichloro aniline (7.90g, 0.02 mol) and triethylamine (2.1 g) were placed in a round bottomed flask having

a Liebig condenser carrying calcium chloride guard tube. The contents were heated for two hours on a boiling water bath. On keeping overnight triethylamine hydrochloride separated as solid. It was filtered and contents concentrated when crystals separated out. Two crystallizations from ethanol gave shining white needles. Yield: 62 %, M.P.: 164^{0}C, Anal. Calculated for $C_{18}H_{14}Cl_2N_2O$; M.W. 345; Calcd. C:62.6; H:4.1; Cl:20.6; N: 8.1, O: 4.6; found C:62.4; H:4.0; Cl:20.5; N: 8.2, O: 4.3; *IR[KBr]* V_{max} Cm^{-1} *:* 3280-3050 (C-H stretching , aromatic), 2955 and 2890 (C-H Stretching, aliphatic (asymmetric) and C-H stretching , aliphatic (symmetric), 2215(C-N stretching), 1655(C=C stretching , benzene ring), 1645 C=O (stretching, tertiary amide), 1615, 1575, 1455, (C=C ring stretching), 1050, 750, (2, 3-disubstituted benzene).

SCHEME-I

(The reaction scheme for the complete synthesis of compounds)



Synthesis of 1-[(2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7]:

A mixture of N-cinnamoyl-N-2'-cyanoethyl - 2, 3-dichloroaniline (0.345 g; 0.001 mol), 2-[(N-cinnamoyl) 2, 3-dichloroanilido] acetohydrazide (0.392g; 0.001 mol), dioxane (3 ml), and glacial acetic acid (2 drops) was refluxed for seven hours. The solid which separated during the course of heating was filtered under suction and purified by washing thrice with hot ethanol, when the pyrazoline was obtained as yellow needles. Yield: 56%, M.P.: 259^0C, M.W.: 719, Anal. Calculated for $C_{36}H_{27}Cl_4N_5O_3$ C: 60.1, H:3.8, Cl: 19.7; N: 9.7, O: 6.7; found C: 60.0, H:3.6, Cl: 19.6; N: 9.4, O: 6.5; U.V. [($\lambda^{Et\,OH}_{Max}$ nm), log ε]: 216.5 (4.98), 317.8 (4.75). *IR[KBr]* V_{max} Cm^{-1} **:** 3300-2870 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2260 (C=N stretching), 1655 [C=O and N-H (amide)] , 1580 (C=N stretching), 1570, 1490, 1430 (C=C ring stretching , aromatic), 1050, 840, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-$d_{6,}$): 2.38-2.52 (2H, s, CH_2), 3.5-3.9 (3H, s, CH_3), 4.25-4.50(1H, s, NH), 6.90-7.50 (13H, m, ArH). 3.25 (1H, dd, J_{AM} = 18 $H_{Z,}$ J_{AX} = 4.60 H_Z, C_4- H_A of pyrazoline ring). 3.95 (1H, dd J_{MA} = 17.85 Hz, J_{MX} = 13.65 Hz, C_4-H_M of pyrazoline ring) , 4.75 (1H, d, J = 16.18 Hz COCH _geminal proton), 5.62 (1H, dd J_{MX} 12.85 $H_{Z\,,}$ J_{AX} = 4.64 Hz, C_5-H_X of pyrazoline ring). Synthetic sequence for new pyrazolines has been outlined in scheme-I.

Some characteristics of the synthesized compounds are shown in table-I. Analytical and spectral data (U.V., I.R., ^{1}H –NMR) confirmed the structures of the new compounds.

1-[(2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7a]:

Yield: 56%, M.P.: 259^0C, M.W.: 719, Anal. Calculated for $C_{36}H_{27}Cl_4N_5O_3$ C: 60.1, H:3.8, Cl: 19.7; N: 9.7, O: 6.7; found C: 60.0, H:3.6, Cl: 19.6; N: 9.4, O: 6.5; U.V. [($\lambda^{Et\,OH}_{Max}$ nm), log ε]: 216.5 (4.98), 317.8 (4.75). *IR[KBr]* V_{max} Cm^{-1} **:** 3300-2870 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2260 (C≡N stretching), 1655 [C=O and N-H (amide)] , 1580 (C=N stretching), 1570, 1490, 1430 (C=C ring stretching , aromatic), 1050, 840, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-$d_{6,}$): 2.38-2.52 (2H, s, CH_2), 3.5-3.9 (3H, s, CH_3), 4.25-4.50(1H, s, NH), 6.90-7.50 (13H, m, ArH). 3.25 (1H, dd, J_{AM} = 18 $H_{Z,}$ J_{AX} = 4.60 H_Z, C_4- H_A of pyrazoline ring). 3.95 (1H, dd J_{MA} = 17.85 Hz, J_{MX} = 13.65 Hz, C_4-H_M of pyrazoline ring) , 4.75 (1H, d, J = 16.18 Hz COCH geminal proton), 5.62 (1H, dd J_{MX} 12.85 $H_{Z\,,}$ J_{AX} = 4.64 Hz, C_5-H_X of pyrazoline ring).

1- [(o-methyl) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7b]:

Yield: 53%, M.P.: 276^0C, M.W.: 733, Anal. Calculated for $C_{37}H_{29}Cl_4N_5O_{3,}$ C: 60.6, H:4.0, Cl: 19.4; N: 9.5, O: 6.5; found C: 60.4, H:4.0, Cl: 19.3; N: 9.3, O: 6.4; U.V. [($\lambda^{Et\,OH}_{M\,ax}$ nm), log ε]: 212.4(4.80), 318.2 (4.85). *IR[KBr]* V_{max} Cm^{-1} **:** 3300-2890 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond) (II) C-H stretching , aromatic (iii)C-H stretching, aliphatic], 2245(C≡N stretching), 1660 [C=O and N-H (amide)] , 1590 (C=N stretching), 1575, 1470, 1420 (C=C ring stretching , aromatic), 1060, 825, (C-Cl stretching , 2,3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-$d_{6,}$): 2.25-2.49 (2H, s, CH_2), 4.20-4.35(1H, s, NH), 6.95-7.40 (13H, m, ArH). 3.15 (1H, dd, J_{AM} = 16 $H_{Z,}$ J_{AX} =

4.65H_Z, C_4- H_A of pyrazoline ring). 3.95 (1H, dd J_{MA} = 17.90 Hz, J_{MX} = 13.85 Hz, C_4-H_M of pyrazoline ring) , 4.66(1H, d, J = 16.45 Hz COCH geminal proton), 5.75 (1H, dd J_{MX} 12.45 H_Z , J_{AX} = 4.50 Hz, C_5-H_X of pyrazoline ring).

1- [(m-methyl) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7c]:

Yield: 58%, M.P.: 262^{0}C, M.W.: 733, Anal. Calculated for $C_{37}H_{29}Cl_4N_5O_3$, C: 60.6, H:4.0, Cl: 19.4; N: 9.5, O: 6.5; found C: 60.5, H:4.0, Cl: 19.2; N: 9.4, O: 6.3; U.V. [($\lambda^{Et\,OH}_{M\,ax}$ nm), log ε]: 215.5(4.85), 318.6 (4.80). *IR[KBr]* V_{max} Cm^{-1} **:** 3300-2890 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond) (II) C-H stretching , aromatic (iii)C-H stretching, aliphatic], 2250(C≡N stretching), 1665 [C=O and N-H (amide)] , 1590 (C=N stretching), 1570, 1475, 1425 (C=C ring stretching , aromatic), 1065, 820, (C-Cl stretching , 2,3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 2.20-2.45 (2H, s, CH_2), 4.25-4.40(1H, s, NH), 6.90-7.45 (13H, m, ArH). 3.18 (1H, dd, J_{AM} = 16 H_Z, J_{AX} = 4.60H_Z, C_4- H_A of pyrazoline ring). 3.90 (1H, dd J_{MA} = 17.95 Hz, J_{MX} = 13.80 Hz, C_4-H_M of pyrazoline ring) , 4.65(1H, d, J = 16.40 Hz COCH geminal proton), 5.70 (1H, dd J_{MX} 12.40 H_Z , J_{AX} = 4.60 Hz, C_5-H_X of pyrazoline ring).

1- [(p-methyl) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-benzoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7d]:

Yield: 55%, M.P.: 271^{0}C, M.W.: 733, Anal. Calculated for $C_{37}H_{29}Cl_4N_5O_3$, C: 60.6, H:4.0, Cl: 19.4; N: 9.5, O: 6.5; found C: 60.2, H:4.1, Cl: 19.4; N: 9.4, O: 6.4; U.V. [($\lambda^{Et\,OH}_{M\,ax}$ nm), log ε]: 212.8(4.75), 318.5 (4.85). *IR[KBr]* V_{max} Cm^{-1} **:** 3300-2880 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond) (II) C-H stretching , aromatic (iii)C-H stretching,aliphatic], 2240(C≡N stretching), 1655 [C=O and N-H (amide)] , 1595 (C=N stretching), 1575, 1465, 1430 (C=C ring stretching , aromatic), 1055, 830, (C-Cl stretching , 2,3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 2.23-2.40 (2H, s, CH_2), 4.20-4.45(1H, s, NH), 6.85-7.45 (13H, m, ArH). 3.20 (1H, dd, J_{AM} = 16 H_Z, J_{AX} = 4.65H_Z, C_4- H_A of pyrazoline ring). 3.85 (1H, dd J_{MA} = 17.90 Hz, J_{MX} = 13.85 Hz, C_4-H_M of pyrazoline ring) , 4.60(1H, d, J = 16.40 Hz COCH geminal proton), 5.80 (1H, dd J_{MX} 12.45 H_Z , J_{AX} = 4.55 Hz, C_5-H_X of pyrazoline ring).

1- [(o-chloro) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7e]:

Yield: 51%, M.P.: 263^{0}C, M.W.: 753.5, Anal. Calculated for $C_{36}H_{27}Cl_5N_5O_3$, C: 57.3, H:3.6, Cl: 23.6; N: 9.3, O: 6.4; found C: 57.2, H:3.5, Cl: 23.4; N: 9.2, O: 6.2; U.V. [($\lambda^{Et\,OH}_{Max}$ nm), log ε]: 212.8 (5.20), 316.4 (5.24). *IR[KBr]* V_{max} Cm^{-1} **:** 3300-3110[broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2270(C≡N stretching), 1670 [C=O and N-H (amide)] , 1560 (C=N stretching), 1540, 1495, 1450 (C=C ring stretching , aromatic), 1090, 870, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 3.15-3.25 (2H, s, CH_2), 4.17-4.45(1H, s, NH), 6.90-7.25 (13H, m, ArH). 3.15 (1H, dd, J_{AM} = 18 H_Z, J_{AX} = 4.65 H_Z, C_4- H_A of pyrazoline ring). 4.15 (1H, dd J_{MA} = 18.20 Hz, J_{MX} = 13.95 Hz, C_4-H_M of pyrazoline ring) , 4.70 (1H, d, J = 16.25 Hz COCH geminal proton), 5.40 (1H, dd J_{MX} 13.25 H_Z , J_{AX} = 5.20 Hz, C_5-H_X of pyrazoline ring).

1- [(m-chloro) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7f]:

Yield: 58%, M.P.: 260^{0}C, M.W.: 753.5, Anal. Calculated for $C_{36}H_{27}Cl_5N_5O_3$, C: 57.3, H:3.6, Cl: 23.6; N: 9.3, O: 6.4; found C: 57.3, H:3.4, Cl: 23.5; N: 9.1, O: 6.3; U.V. [($\lambda^{Et\,OH}_{Max}$ nm), log ε]: 213.2 (5.10), 315.5 (5.28). *IR[KBr] V_{max} Cm^{-1}* **:** 3300-3120 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2285(C≡N stretching), 1680 [C=O and N-H (amide)] , 1550 (C=N stretching), 1550, 1490, 1465 (C=C ring stretching , aromatic), 1095, 875, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 3.20-3.35 (2H, s, CH_2), 4.22-4.40(1H, s, NH), 7.10-7.30 (13H, m, ArH). 3.10 (1H, dd, J_{AM} = 18 H_Z, J_{AX} = 4.80 H_Z, C_4- H_A of pyrazoline ring). 4.30 (1H, dd J_{MA} = 18.25 Hz, J_{MX} = 13.80 Hz, C_4-H_M of pyrazoline ring) , 4.80 (1H, d, J = 16.20 Hz COCH geminal proton), 5.45 (1H, dd J_{MX} 13.45 H_Z, J_{AX} = 5.30 Hz, C_5-H_X of pyrazoline ring).

1- [(p-chloro) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7g]:

Yield: 55%, M.P.: 271^{0}C, M.W.: 753.5, Anal. Calculated for $C_{36}H_{27}Cl_5N_5O_3$, C: 57.3, H:3.6, Cl: 23.6; N: 9.3, O: 6.4; found C: 57.0, H:3.2, Cl: 23.5; N: 9.3, O: 6.1; U.V. [($\lambda^{Et\,OH}_{Max}$ nm), log ε]: 213.3 (5.25), 315.1 (5.22). *IR[KBr] V_{max} Cm^{-1}* **:** 3300-3105[broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2250(C≡N stretching), 1650 [C=O and N-H (amide)] , 1550 (C=N stretching), 1560, 1475, 1430 (C=C ring stretching , aromatic), 1075, 860, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 3.15-3.25 (2H, s, CH_2), 4.17-4.35(1H, s, NH), 6.85-7.10 (13H, m, ArH). 3.15 (1H, dd, J_{AM} = 18 H_Z, J_{AX} = 4.75 H_Z, C_4- H_A of pyrazoline ring). 4.20 (1H, dd J_{MA} = 18.20 Hz, J_{MX} = 13.90 Hz, C_4-H_M of pyrazoline ring) , 4.75 (1H, d, J = 16.22 Hz COCH geminal proton), 5.30 (1H, dd J_{MX} 13.20 H_Z, J_{AX} = 5.25 Hz, C_5-H_X of pyrazoline ring).

1- [(o-methoxy) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7h]:

Yield: 65%, M.P.: 256^{0}C, M.W.: 749, Anal. Calculated for $C_{37}H_{29}Cl_4N_5O_4$ C: 59.3, H:3.9, Cl: 19.0; N: 9.3, O: 8.5; found C: 59.2, H:3.7, Cl: 19.0; N: 9.2, O: 8.3; U.V. [($\lambda^{Et\,OH}_{Max}$ nm), log ε]: 214.2 (5.15), 318.2(4.90). *IR[KBr] V_{max} Cm^{-1}* **:** 3300-2860 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2270(C≡N stretching), 1645 [C=O and N-H (amide)] , 1580 (C=N stretching), 1575, 1460, 1445 (C=C ring stretching , aromatic), 1040, 830, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 2.30-2.55 (2H, s, CH_2), 4.25-4.55(1H, s, NH), 6.80-7.10 (13H, m, ArH). 3.20 (1H, dd, J_{AM} = 17 H_Z, J_{AX} = 4.55 H_Z, C_4- H_A of pyrazoline ring). 3.90 (1H, dd J_{MA} = 17.95 Hz, J_{MX} = 13.85 Hz, C_4-H_M of pyrazoline ring) , 4.80 (1H, d, J = 16.20 Hz COCH geminal proton), 5.45 (1H, dd J_{MX} 11.95 H_Z, J_{AX} = 4.90 Hz, C_5-H_X of pyrazoline ring).

1- [(m-methoxy) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7i]:

Yield: 60%, M.P.: 265^{0}C, M.W.: 749, Anal. Calculated for $C_{37}H_{29}Cl_4N_5O_4$ C: 59.3, H:3.9, Cl: 19.0; N: 9.3, O: 8.5; found C: 59.1, H:3.8, Cl: 19.0; N: 9.1, O: 8.4; U.V. [($\lambda^{Et\,OH}_{Max}$ nm),

log ε]: 214.1 (5.10), 318.5(4.95). *IR[KBr] V_{max} Cm^{-1}* **:** 3300-2880 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2260(C≡N stretching), 1655 [C=O and N-H (amide)] , 1585 (C=N stretching), 1565, 1450, 1435 (C=C ring stretching , aromatic), 1045, 820, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 2.20-2.35 (2H, s, CH_2), 4.20-4.50(1H, s, NH), 6.95-7.20 (13H, m, ArH). 3.25 (1H, dd, J_{AM} = 18 H_Z, J_{AX} = 4.50 H_Z, C_4- H_A of pyrazoline ring). 3.95 (1H, dd J_{MA} = 17.90 Hz, J_{MX} = 13.70 Hz, C_4-H_M of pyrazoline ring) , 4.70 (1H, d, J = 16.25 Hz COCH geminal proton), 5.65 (1H, dd J_{MX} 12.20 H_Z , J_{AX} = 4.95 Hz, C_5-H_X of pyrazoline ring).

1- [(p-methoxy) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7j]:

Yield: 71%, M.P.: 260^{0}C, M.W.: 749, Anal. Calculated for C_{37} H_{29} Cl_4 N_5 O_4 C: 59.3, H:3.9, Cl: 19.0; N: 9.3, O: 8.5; found C: 59.3, H:3.8, Cl: 19.1; N: 9.1, O: 8.1; U.V. [($\lambda^{Et\,OH}_{Max}$ nm), log ε]: 215.1 (5.0), 318.5(4.80). *IR[KBr] V_{max} Cm^{-1}* **:** 3300-2850 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2260(C≡N stretching), 1655 [C=O and N-H (amide)] , 1585 (C=N stretching), 1565, 1440, 1425 (C=C ring stretching , aromatic), 1050, 840, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 2.35-2.50 (2H, s, CH_2), 4.15-4.35(1H, s, NH), 6.70-7.15 (13H, m, ArH). 3.25 (1H, dd, J_{AM} = 18 H_Z, J_{AX} = 4.50 H_Z, C_4- H_A of pyrazoline ring). 3.85 (1H, dd J_{MA} = 18.10 Hz, J_{MX} = 13.75 Hz, C_4-H_M of pyrazoline ring) , 4.85 (1H, d, J = 16.30 Hz COCH geminal proton), 5.55 (1H, dd J_{MX} 12.10 H_Z , J_{AX} = 4.70 Hz, C_5-H_X of pyrazoline ring).

1- [(p-floro) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7k]:

Yield: 61%, M.P.: 245^{0}C, M.W.: 737, Anal. Calculated for C_{36} H_{26} Cl_4 $F_1$$N_5$ O_3 C: 58.6, H:3.5, Cl: 19.3; N: 9.5, O: 6.5; F: 2.6 found C: 58.4, H:3.4, Cl: 19.5; N: 9.4, O: 6.5; F: 2.5 U.V. [($\lambda^{Et\,OH}_{Max}$ nm), log ε]: 217.6 (4.99), 318.5 (4.80). *IR[KBr] V_{max} Cm^{-1}* **:** 3300-2850 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2255(C≡N stretching), 1670 [C=O and N-H (amide)] , 1585 (C=N stretching), 1575, 1455, 1420 (C=C ring stretching , aromatic), 1050, 865, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 2.20-2.40 (2H, s, CH_2), 4.20-4.60(1H, s, NH), 6.80-7.15 (13H, m, ArH). 3.19 (1H, dd, J_{AM} = 18 H_Z, J_{AX} = 4.45 H_Z, C_4- H_A of pyrazoline ring). 3.97 (1H, dd J_{MA} = 17.95Hz, J_{MX} = 13.60 Hz, C_4-H_M of pyrazoline ring) , 4.80 (1H, d, J = 16.45 Hz COCH geminal proton), 5.35 (1H, dd J_{MX} 12.80 H_Z , J_{AX} = 4.45 Hz, C_5-H_X of pyrazoline ring).

1- [(o-bromo) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7l]:

Yield: 58%, M.P.: 264^{0}C, M.W.: 799, Anal. Calculated for C_{36} H_{26} Br_1 Cl_4 N_5 O_3 C: 54.1, H:3.3, Cl: 17.8; N: 8.8, O: 6.0; Br: 10; found C: 54.0, H:3.2, Cl: 17.7; N: 8.7, O: 6.1; Br: 10.1; U.V. [($\lambda^{Et\,OH}_{Max}$ nm), log ε]: 212.6 (4.96), 318.2 (4.75). *IR[KBr] V_{max} Cm^{-1}* **:** 3300-2880 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2240(C≡N stretching), 1630 [C=O and N-H (amide)] , 1560 (C=N stretching), 1610, 1530, 1480 (C=C ring stretching ,

aromatic), 1075, 830, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 2.25-2.55 (2H, s, CH_2), 4.25-4.50(1H, s, NH), 6.85-7.20 (13H, m, ArH). 3.22 (1H, dd, J_{AM} = 18 H_Z, J_{AX} = 4.70 H_Z, C_4- H_A of pyrazoline ring). 4.20 (1H, dd J_{MA} = 17.80 Hz, J_{MX} = 13.40 Hz, C_4-H_M of pyrazoline ring) , 4.65 (1H, d, J = 16.55 Hz COCH geminal proton), 5.75 (1H, dd J_{MX} 13.20 H_Z , J_{AX} = 4.60 Hz, C_5-H_X of pyrazoline ring).

1- [(o-ethoxy) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7m]:

Yield: 62%, M.P.: 269^{0}C, M.W.: 764, Anal. Calculated for $C_{38}H_{31}Cl_4N_5O_4$ C: 59.7, H:4.1, Cl: 18.6; N: 9.2, O: 8.4; found C: 59.6, H:4.0, Cl: 18.5; N: 9.3, O: 8.3; U.V. [($\lambda^{Et\,OH}_{Max}$ nm), log ε]: 212.5 (4.90), 318.1 (4.85). *IR[KBr]* V_{max} Cm^{-1} **:** 3300-2910 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2250(C≡N stretching), 1640 [C=O and N-H (amide)] , 1570 (C=N stretching), 1570, 1460, 1440 (C=C ring stretching , aromatic), 1070, 875, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 2.35-2.50 (2H, s, CH_2), 4.20-4.45(1H, s, NH), 6.85-7.25 (13H, m, ArH). 3.20 (1H, dd, J_{AM} = 18 H_Z, J_{AX} = 4.50 H_Z, C_4- H_A of pyrazoline ring). 3.90 (1H, dd J_{MA} = 17.90 Hz, J_{MX} = 13.55 Hz, C_4-H_M of pyrazoline ring) , 4.65 (1H, d, J = 16.45 Hz COCH geminal proton), 5.45(1H, dd J_{MX} 12.95 H_Z , J_{AX} = 4.65 Hz, C_5-H_X of pyrazoline ring).

1- [(m-ethoxy) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7n]:

Yield: 59%, M.P.: 258^{0}C, M.W.: 764, Anal. Calculated for $C_{38}H_{31}Cl_4N_5O_4$ C: 59.7, H:4.1, Cl: 18.6; N: 9.2, O: 8.4; found C: 59.5, H:4.1, Cl: 18.4; N: 9.1, O: 8.2; U.V. [($\lambda^{Et\,OH}_{Max}$ nm), log ε]: 213.5 (4.95), 318.1 (5.10). *IR[KBr]* V_{max} Cm^{-1} **:** 3300-2900 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2230(C≡N stretching), 1660 [C=O and N-H (amide)] , 1560 (C=N stretching), 1575, 1465, 1445 (C=C ring stretching , aromatic), 1060, 855, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 2.25-2.40 (2H, s, CH_2), 4.20-4.45(1H, s, NH), 6.90-7.20 (13H, m, ArH). 3.40 (1H, dd, J_{AM} = 18 H_Z, J_{AX} = 4.40 H_Z, C_4- H_A of pyrazoline ring). 3.70 (1H, dd J_{MA} = 17.80 Hz, J_{MX} = 13.70 Hz, C_4-H_M of pyrazoline ring) , 4.60 (1H, d, J = 16.20 Hz COCH geminal proton), 5.40(1H, dd J_{MX} 12.85 H_Z , J_{AX} = 4.55 Hz, C_5-H_X of pyrazoline ring).

1- [(p-ethoxy) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7o]:

Yield: 63%, M.P.: 263^{0}C, M.W.: 764, Anal. Calculated for $C_{38}H_{31}Cl_4N_5O_4$ C: 59.7, H:4.1, Cl: 18.6; N: 9.2, O: 8.4; found C: 59.6, H:4.0, Cl: 18.3; N: 9.1, O: 8.3; U.V. [($\lambda^{Et\,OH}_{Max}$ nm), log ε]: 213.8 (4.92), 318.7 (4.85). *IR[KBr]* V_{max} Cm^{-1} **:** 3300-2920 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2240(C≡N stretching), 1650 [C=O and N-H (amide)] , 1550 (C=N stretching), 1595, 1480, 1440 (C=C ring stretching , aromatic), 1050, 830, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 2.30-2.45 (2H, s, CH_2), 4.15-4.55(1H, s, NH), 6.80-7.20 (13H, m, ArH). 3.30 (1H, dd, J_{AM} = 19 H_Z, J_{AX} = 4.70 H_Z, C_4- H_A of pyrazoline ring). 3.95 (1H, dd J_{MA} = 17.65 Hz, J_{MX} = 13.60Hz, C_4-H_M

of pyrazoline ring) , 4.75 (1H, d, J = 16.30 Hz COCH geminal proton), 5.60(1H, dd J_{MX} 12.70 H_Z , J_{AX} = 4.75 Hz, C_5-H_X of pyrazoline ring).

1- [(m-bromo) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7s]:

Yield: 55%, M.P.: 261^{0}C, M.W.: 799, Anal. Calculated for $C_{36}H_{26}Br_1Cl_4N_5O_3$ C: 54.1, H:3.3, Cl: 17.8; N: 8.8, O: 6.0; Br: 10; found C: 54.1, H:3.1, Cl: 17.5; N: 8.5, O: 6.0; Br: 10.2; U.V. [($\lambda^{Et\ OH}_{Max}$ nm), log ε]: 212.9 (4.92), 317.8 (4.85). *IR[KBr] V_{max} Cm^{-1}* **:** 3300-2890 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2245(C≡N stretching), 1650 [C=O and N-H (amide)] , 1590 (C=N stretching), 1590, 1540, 1495 (C=C ring stretching , aromatic), 1060, 840, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-d_6,): 2.21-2.50 (2H, s, CH_2), 4.20-4.40(1H, s, NH), 6.85-7.20 (13H, m, ArH). 3.22 (1H, dd, J_{AM} = 18 H_Z, J_{AX} = 4.50 H_Z, C_4- H_A of pyrazoline ring). 4.10 (1H, dd J_{MA} = 17.80 Hz, J_{MX} = 13.30 Hz, C_4-H_M of pyrazoline ring) , 4.50 (1H, d, J = 16.20 Hz COCH geminal proton), 5.65 (1H, dd J_{MX} 13.10 H_Z , J_{AX} = 4.65Hz, C_5-H_X of pyrazoline ring).

Table-I

(Unsubstituted / Substituted) *1-[(2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) -2, 3-dichloroanilino)]-5- phenyl pyrazoline.*

CS. No.	***R***	***Color***	***M.P. (˚C)***	***Yield (%)***	***M.W.***	***Molecular Formula***
7a.	H	Yellow	259	56	719	$C_{36}H_{27}Cl_4N_5O_3$
7b.	CH_3(o)	Cream	276	53	733	$C_{37}H_{29}Cl_4N_5O_3$
7c.	CH_3(m)	Light Yellow	262	58	733	$C_{37}H_{29}Cl_4N_5O_3$
7d.	CH_3(p)	Light Yellow	271	55	733	$C_{37}H_{29}Cl_4N_5O_3$
7e.	Cl(o)	white	263	51	753.5	$C_{36}H_{27}Cl_5N_5O_3$
7f.	Cl(m)	Light Yellow	260	58	753.5	$C_{36}H_{27}Cl_5N_5O_3$
7g.	Cl(p)	Cream	271	55	753.5	$C_{36}H_{27}Cl_5N_5O_3$
7h.	O-CH_3(o)	Yellow	256	65	749	$C_{37}H_{29}Cl_4N_5O_4$
7i.	O-CH_3(m)	White	265	60	749	$C_{37}H_{29}Cl_4N_5O_4$
7j.	O-CH_3(p)	Cream	260	71	749	$C_{37}H_{29}Cl_4N_5O_4$
7k.	F(p)	Yellow	245	47	737	$C_{36}H_{26}Cl_4N_5O_3F_1$
7l.	Br(o)	Dark brown	264	58	799	$C_{36}H_{26}Cl_4N_5O_3Br_1$
7m.	O-C_2H_5 (o)	L. Brown	269	62	764	$C_{38}H_{31}Cl_4N_5O_4$
7n.	O-C_2H_5(m)	Brown	258	59	764	$C_{38}H_{31}Cl_4N_5O_4$
7o.	O-C_2H_5 (p)	Brown	263	63	764	$C_{38}H_{31}Cl_4N_5O_4$
7p.	CO_2H (o)	Brown	252	63	763	$C_{37}H_{27}Cl_4N_5O_5$
7q.	CO_2H (m)	Brown	245	58	763	$C_{37}H_{27}Cl_4N_5O_5$
7r.	CO_2H (p)	L. brown	256	53	763	$C_{37}H_{27}Cl_4N_5O_5$
7s.	Br(m)	Brown	261	55	799	$C_{36}H_{26}Cl_4N_5O_3Br_1$
7t.	Br(p)	Brown	257	51	799	$C_{36}H_{26}Cl_4N_5O_3Br_1$

All compounds gave satisfactory elemental analysis.

1- [(p-bromo) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline [7t]:

Yield: 52%, M.P.: 256^{0}C, M.W.: 799, Anal. Calculated for $C_{36}H_{26}Br_1Cl_4N_5O_3$ C: 54.1, H:3.3, Cl: 17.8; N: 8.8, O: 6.0; Br: 10; found C: 54.0, H:3.2, Cl: 17.6; N: 8.6, O: 6.1; Br:

10.1; U.V. [($\lambda^{Et\,OH}_{Max}$ nm), log ε]: 212.6 (4.85), 318.1 (4.80). *IR[KBr] V_{max} Cm^{-1}* **:** 3300-2860 [broad band due to (I) N-H stretching, secondary amide (Intra molecular hydrogen bond), (II) C-H stretching , aromatic , (iii) C-H stretching , aliphatic], 2260(C≡N stretching), 1630 [C=O and N-H (amide)] , 1595 (C=N stretching), 1575, 1545, 1465 (C=C ring stretching , aromatic), 1045, 835, (C-Cl stretching , 2, 3-disubstituted aromatic ring). ^{1}H-NMR (250 MHz, δ ppm, DMSO-$d_{6,}$): 2.23-2.45 (2H, s, CH_2), 4.25-4.35(1H, s, NH), 6.80-7.30 (13H, m, ArH). 3.28 (1H, dd, J_{AM} = 18 $H_{Z,}$ J_{AX} = 4.45 H_Z, C_4- H_A of pyrazoline ring). 4.50 (1H, dd J_{MA} = 16.90 Hz, J_{MX} = 13.40 Hz, C_4-H_M of pyrazoline ring) , 4.55 (1H, d, J = 16.30 Hz COCH geminal proton), 5.70 (1H, dd J_{MX} 13.0 $H_{Z\,,}$ J_{AX} = 4.62Hz, C_5-H_X of pyrazoline ring).

Most of the pyrazolines are high melting point and light yellow or cream colored solids. The data of new products are furnished in table- I.

Table-II:Tuberculostatic Activity of new pyrazolines

S.No.	***Compounds***	***Growth at conc. [mg/mL]***	
		10	***100***
7a.	*1-[(2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N-cinnamoyl) -2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	*0*
7b.	*1- [(o-methyl) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	+
7c.	*1- [(m-methyl) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	0
7d.	*1- [(p-methyl) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	+
7e.	*1- [(o-chloro) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	*0*
7f.	*1- [(m-chloro) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	+
7g.	*1- [(p-chloro) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	+
7h.	*1- [(o-methoxy) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	+
7i.	*1- [(m-methoxy) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	+
7j.	*1- [(p-methoxy) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	*0*
7k.	*1- [(p-floro) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline .*	+	+
7l.	*1- [(o-bromo) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	+
7m.	*1- [(o-ethoxy) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	*0*
7n.	*1- [(m-ethoxy) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	+
7o.	*1- [(p-ethoxy) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	+
7s.	*1- [(m-bromo) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	+
7t.	*1- [(p-bromo) -2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) 2, 3-dichloroanilino)]-5- phenyl pyrazoline*	+	+

'+' and '0' indicate presence and inhibition of growth respectively.

Biological Evaluation

Anti-bacterial activity:

Newly synthesized compounds *(7a-t)* have been tested for their *antibacterial activity* against gram positive bacteria *S. albus, S. aureus* and gram negative bacteria *E.Coli* and *Pseudomonas poisonous* by agar plate disc diffusion method at 30 µg/mL concentration. Ampicillin and Tetracycline used as a reference compound. The compound ***(7a, 7c, 7e, 7j, 7m, and 7s)*** shown significant activity and the compound *(7i, 7k, 7t,) have* shown moderate activity.

Anti-fungal activity:

The same compounds were tested for their *antifungal activity* against *Candida albicans, Aspergillus Niger and Alternaria alternata* at concentration of 30 mg/mL using sabouraud dextrose agar media. The compound ***(7b, 7j, 7m, and 7r)*** shown significant activities and compound *(7a, 7f, and 7g)* were found to be moderately active against *Candida albicans and Aspergillus Niger.* All the other compounds did not show significant activity against the fungi at the concentration used.

Tuberculostatic Activity:

Some new compounds have been tested for *antitubercular* activity in-vitro using *Mycobacterium tuberculosis.* The compounds were incorporated into Lowenstein Jensen egg medium having concentrations of 10 and 100 mg/mL and were inoculated with *Mycobacterium tuberculosis,* $H_{27,}$ R_V strains, incubated at 37^0C and observed, weekly for the growth of organism for eight weeks. The compound ***(7a, 7c, 7e, 7j, and 7m)*** inhibited the growth of *Mycobacterium tuberculosis* at 100mg/mL concentration other compounds were found to be inactive. Results are assembled in table-II.

RESULTS AND DISCUSSION

Newly synthesized *1-[(2, 3-dichloroanilinomalonyl)-3-(N-2'-cyanoethyl)-2-(N- cinnamoyl) -2, 3-dichloroanilino)]-5- phenyl pyrazoline have been synthesized by the reaction of* N-cinnamoyl-N-2'-cyanoethyl-2,3-dichloroaniline with 2-[(N-*cinnamoyl*) 2,3-dichloroanilido] acetohydrazide. Pyrazolines are yellow, cream and brown color solids, having high melting points. Identity of these products has been established by elemental analysis and spectral data. Newly synthesized compounds *(7a-t)* have been tested for their *antibacterial activity* against gram positive bacteria *S. albus , S. aureus* and gram negative bacteria *E. Coli* and *Pseudomonas poisonous* .The compound ***(7a, 7c, 7e, 7j, 7m, and 7s)*** shown significant activity and the compound *(7i, 7k, 7t,) have* shown moderate activity. The same compounds were tested for their *antifungal activity* against *Candida albicans, Aspergillus Niger and Alternaria alternata* at concentration of 30 mg/mL using sabouraud dextrose agar media. The compound ***(7b, 7j, 7m, and 7r)*** shown significant activities and compound *(7a, 7f, and 7g)* were found to be moderately active against *Candida albicans and Aspergillus Niger.* All the other compounds did not show significant activity against the fungi at the concentration used. Some new compounds have been tested for *antitubercular* activity in-vitro using *Mycobacterium tuberculosis.* The compounds were incorporated into Lowenstein Jensen egg medium having concentrations of 10 and 100 mg/mL and were inoculated with *Mycobacterium tuberculosis,* $H_{27,}$ Rv strains, incubated at 37^0C and observed, the compound ***(7a, 7c, 7e, 7j, and 7m)*** inhibited the growth of *Mycobacterium tuberculosis* at 100mg/mL concentration other compounds were found to be inactive.

CONCLUSION

Newly synthesized compounds *(7a-t)* have been tested for their ***antibacterial activity*** against gram positive bacteria *S. albus , S. aureus* and gram negative bacteria *E.Coli* and *Pseudomonas poisonous* .The compound ***(7a, 7c, 7e, 7j, 7m, and 7s)*** shown significant activity and the compound *(7i, 7k, 7t,) have* shown moderate activity. The same compounds were tested for their ***antifungal activity*** against *Candida albicans, Aspergillus Niger and Alternaria alternata* at concentration of 30 mg/mL using sabouraud dextrose agar media. The compound ***(7b, 7j, 7m, and 7r)*** shown significant activities and compound *(7a, 7f, and 7g)* were found to be moderately active against *Candida albicans and Aspergillus Niger.* All the other compounds did not show significant activity against the fungi at the concentration used. Some new compounds have been tested for ***antitubercular*** activity in-vitro using *Mycobacterium tuberculosis.* The compounds were incorporated into Lowenstein Jensen egg medium having concentrations of 10 and 100 mg/mL and were inoculated with *Mycobacterium tuberculosis,* $H_{27,}$Rv strains, incubated at 37^0C and observed, the compound ***(7a, 7c, 7e, 7j, and 7m)*** inhibited the growth of *Mycobacterium tuberculosis* at 100mg/mL concentration other compounds were found to be inactive.

Acknowledgement
The authors are thankful to Director, C.D.R.I. Lucknow (U.P.), for elemental analysis, Director, Tuberculosis Research Centre, Amargadh (Gujrat), for testing tuberculostatic activity and Director, D.R.D.E. Gwalior (M.P.), for spectral studies, and Director, Cancer Hospital and Research Institute, G.R. Medical College and Birla Institute of Medical Research, Gwalior (M. P.), for Biological activities. We are also grateful to principal SMS Government Model Science College, Gwalior (M.P), for providing research facilities.

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