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A convenient route for the synthesis and characterization of novel substituted azo-coumarins and Schiff's bases

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ABSTRACT

A simple,rapid,gradient,accurate condensation reaction of 2-methoxy-5-methyl malon anilic acid (2a) with different substituted phenyl Azo-Salicylaldehydes (2a-2j) in the presence of pyridine as a condensing agent. Structures of newly synthesized compounds were established on the basis of their Spectral studies viz: IR, Elemental analysis and Physical properties.

Key words: Substituted azo-coumarins and Schiff's bases, Pyridine, Condensation, Spectral analysis.

INTRODUCTION

Azo-coumarins is a simple oxygen containing heterocyclic compounds of pharmacological interest[1-3], they have been widely used in many practical applications such as coloring fiber,printing systems ,analytical chemistry[4]. Derivatives of azo-coumarin have been found in application as CNS represents antibiotics[5],anti-inflammatory[6], antibacterial[7],antifungal[8] activities. Schiff's bases are widely used for synthetic purposes, it represents a class of compounds having Importance in the field of medicinal & agriculture. Schiff's bases have also possess biochemical and biological activities such as antiviral[9],anticancer[10],antimicrobial[11],antibacteri-al[12]. By various workers several Azo-coumarins and Schiff's bases have been synthesized in our laboratory[13-19].

As a continuation of our previous work here in the present study we have synthesized a Novel series of Azo - coumarins and Schiff's bases by the condensation of 2 - methoxy-5-methyl malon anilic acid and (R) azo-salicylaldehydes in presence of pyridine as a catalyst. The biological and Analytical properties of the synthesized compounds are under study.

EXPERIMENTAL

Material

All the used chemicals in the synthesis were of Sigma-Aldrich Company. All melting points were determined in open capillary tubes and were uncorrected. All newly synthesized compounds were recrystallized by absolute ethanol 99%. Purities of the compounds checked by TLC on silica-gel-coated AI plates (E-Merck).

IR spectra (cm^{-1}) were recorded on Perkin-Elmer spectrum RX-1 FT-IR spectrophotometer at Central Drug Research Institute (CDRI), Lucknow by Kbr-disc method. The physical and analytical data, molecular formula, molecular weight, melting point, colour, yield% are recorded in Table-1 and spectral analysis are recorded in Table-2.

Synthesis of N-(2-methoxy-5-methyl)phenyl malonamic acid and N:N^{I}-di(2-methoxy-5-methyl) phenyl malonamide (1a,5a)

To primary amine (0.025 mole), diethyl malonate (0.05 mole) was added with the catalyst dimethyl formamide , refluxed for 45-60 minutes , after cooling , the solid separated was recrystallised by ethanol ,on analysis it was found to be N:N^{I} - di (2-methoxy-5-methyl)phenyl malonamide (**5a**) ,

filtered and add ethanol (20 ml) with a solution of Na_2CO_3 (20 ml) , take hydrolysis of the reaction mixture for about 30-45 minutes , filtered, to the filtrate HCI was added . The solid thus separated, filtered washed with dis. water, recrystallized and was Identified to be N(2-methoxy-5-methyl) phenyl malonamic acid (**1a**).

Synthesis of 2-hydroxy-5-(R) phenyl azo benzaldehyde (2a-2j).

To the substituted aniline (0.025 mole) was diazotised by adding concentrated HCl (8ml) in (7ml) water maintained the temperature at 0°C in an ice-bath, then added Sodium Nitritesolution (8ml) with stirring, solution of salicylald ehyde (0.025 mole) in 2N NaOH (20 ml) was added with constant stirring to the above diazotised solution . The solid is started separating out immediately was filtered,washed with cold water ,recrystallized from hot ethanol.

Synthesis of 6-(R)-phenyl azo-coumarin-3-carboxy-(2-methoxy-5-methyl) anilide (3a-3j) and 2-hydroxy-5(R)phenyl-azo-benzylidine-(2-methoxy-5-methyl)aniline (4a-4j) A mixture of N (2-methoxy-5-methyl) phenyl malonamic acid (0.001 mole; 1a) and 2-hydroxy -5(R) phenyl-azo benzaldehyde (0.001 mole;2a-2j) in equimolar quantities (1:1),with a trace of pyridine was added to it. The reaction mixture was heated for 4-hours in an oil-bath maintained temperature at 104° to 112°C, the mixture was first melted to a liquid and then soon set to a solid, cooling and then digested with the solution of $NaHCO_3$, washed with water several times, the Schiff's bases was removed by the extraction with hot ethanol (10 ml), residue was recrystallised from hot absolute ethanol, Schiff's bases was also recrystallised from absolute ethanol.

RESULTS AND DISCUSSION

The Infra-red Spectra of newly synthesized compounds have been recorded in the frequency region 4000-450 cm^{-1} these are furnished in Table-2. The Infra-red (KBr) spectrum of the compounds 6(R)-phenyl azo – coumarin-3-carboxy-(2-methoxy-5-methyl) anilide[3a-3d] shows absorption in the range 1552.0-1544.7 cm^{-1} indicating the presence of aromatic C=O, absorption in the range 1493.4-1491.1 cm^{-1} shows N=N stretching vibrations and absorption in the range 1609.9-1594.6 cm^{-1} reveals -CONH stretching vibrations, -C=O stretching vibrations were obtained between 1730.5-1715.1 cm^{-1} and absorption in the range 3449.9-3418.0 cm^{-1} confirms the presence of –NH. All of these observations are agreed with the assigned structures of compounds 3a-3d and other compounds (3e-3j). The IR (Kbr) Spectrum of 2-hydroxy-5-(R)phenylazo-benzylidine-(2-methoxy-5-methyl)aniline[4a-4d] showed absorption in the range 1541.8-1538.7 cm^{-1} indicates aromatic -C=C, absorption in the range 2364.3-2360.1 cm^{-1} reveals -HC=N , absorption in the range 3424.2-3411.5 cm^{-}

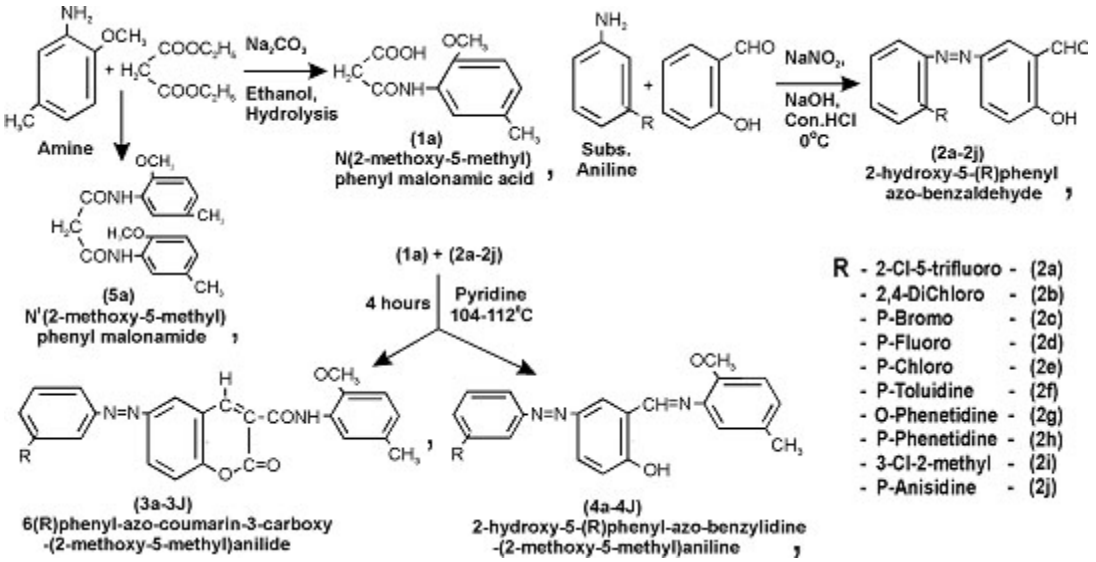

Table 1 : Physical and Analytical data of synthesized compounds (1a,2a-2j,3a-3j,4a-4j,5a)

Compounds codes	Molecular Formula	Molecular Weight	Melting Point 0°C	Yield %	Colour	% Analytical data C cal.%	(Found)%	H cal.%	(Found)%	N cal.%	(Found)%
1a	$C_{11}H_{13}N_1O_4$	223.23	104	40.72	Tinge of rose	59.18	59.20	5.87	5.88	06.27	06.30
2a	$C_{14}H_8N_2O_2Cl_1F_3$	330.08	119	73.25	Light sunset	51.06	51.08	2.73	2.74	08.49	08.53
2b	$C_{13}H_9N_2O_2Cl_2$	296.14	118	59.70	Milk toffee	52.72	52.74	3.06	3.08	09.46	09.49
2c	$C_{13}H_{10}N_2O_2Br_1$	306.15	204	67.33	Light sporty yellow	51.00	51.03	3.30	3.31	09.15	09.19
2d	$C_{13}H_{10}N_2O_2F_1$	245.23	155	65.47	Light yellow	63.67	63.69	4.11	4.13	11.42	11.46
2e	$C_{13}H_{10}N_2O_2Cl_1$	261.69	187	59.95	Light sporty yellow	59.66	59.67	3.85	3.87	10.70	10.74
2f	$C_{14}H_{13}N_2O_2$	241.27	136	50.37	Oranguish yellow	69.69	69.72	5.43	5.44	11.61	11.65
2g	$C_{15}H_{15}N_2O_3$	271.30	83	59.33	Coffee brown	66.40	66.41	5.57	5.58	10.32	10.34
2h	$C_{15}H_{15}N_2O_3$	271.30	126	51.64	Light dirty yellow	66.40	66.42	5.57	5.59	10.32	10.36
2i	$C_{14}H_{12}N_2O_2Cl_1$	275.71	147	59.13	Dark dirty yellow	60.99	61.01	4.38	4.39	10.16	10.19
2j	$C_{14}H_{13}N_2O_3$	257.27	112	63.13	Rust brown	65.36	65.38	5.09	5.11	10.89	10.93
3a	$C_{25}H_{18}N_3O_4Cl_1F_3$	516.90	256	42.85	Brillient orange	58.09	58.11	3.51	3.52	08.13	08.17
3b	$C_{24}H_{18}N_3O_4Cl_2$	483.34	233	62.81	Dirty orange	59.64	59.66	3.75	3.77	08.69	08.71
3c	$C_{24}H_{19}N_3O_4Br_1$	493.35	224	59.54	Light orange	58.43	58.44	3.88	3.89	08.52	08.55
3d	$C_{24}H_{19}N_3O_4F_1$	432.44	203	63.24	Light orange	66.66	66.68	4.43	4.44	09.72	09.76
3e	$C_{24}H_{19}N_3O_4Cl_1$	448.90	226	70.24	Orange	64.21	64.23	4.26	4.27	09.36	09.40
3f	$C_{25}H_{22}N_3O_4$	428.47	238	52.15	Light orange	70.08	70.09	5.17	5.18	09.81	09.84
3g	$C_{26}H_{24}N_3O_5$	458.50	224	40.89	Light sunset	68.11	68.12	5.27	5.28	09.16	09.18
3h	$C_{26}H_{24}N_3O_5$	458.50	214	45.95	Light yellow	68.11	68.13	5.27	5.29	09.16	09.20
3i	$C_{25}H_{21}N_3O_4Cl_1$	462.92	209	70.48	Dirty yellow	64.86	64.87	4.57	4.59	09.08	09.11
3j	$C_{25}H_{22}N_3O_5$	444.47	197	56.87	Sporty yellow	67.55	67.56	4.99	5.01	09.45	09.50
4a	$C_{22}H_{19}N_3O_2Cl_1F_3$	449.87	66	52.07	Dirty yellow	58.73	58.74	4.26	4.28	09.34	09.39
4b	$C_{21}H_{19}N_3O_2Cl_2$	416.32	65	59.92	Brick tone	60.59	60.60	4.60	4.61	10.09	10.12
4c	$C_{21}H_{20}N_3O_2Br_1$	426.33	89	58.03	Red earth	59.16	59.19	4.73	4.74	09.86	09.89
4d	$C_{21}H_{20}N_3O_2F_1$	365.41	91	57.47	Dirty sunrise	69.03	69.04	5.52	5.55	11.50	11.55
4e	$C_{21}H_{20}N_3O_2Cl_1$	381.87	78	45.24	Camp fire	66.05	66.07	5.28	5.30	11.06	11.10
4f	$C_{22}H_{23}N_3O_2$	361.45	72	57.32	Geranium	73.06	73.08	6.14	6.15	11.62	11.66
4g	$C_{23}H_{25}N_3O_3$	391.48	74	57.28	Brown	70.56	70.57	6.44	6.46	10.73	10.75
4h	$C_{23}H_{25}N_3O_3$	391.48	86	54.04	Light sunrise	70.56	70.58	6.44	6.45	10.73	10.77
4i	$C_{22}H_{22}N_3O_2Cl_1$	395.90	62	63.85	Raspberry crush	66.74	66.75	5.60	5.61	10.61	10.63
4j	$C_{22}H_{23}N_3O_3$	377.45	66	59.58	Brown	70.00	70.01	6.14	6.16	11.13	11.17
5a	$C_{19}H_{22}N_2O_4$	342.39	134	32.14	Creamish	66.65	66.67	6.47	6.49	08.18	08.22

[1] indicates the free -OH group, absorption in the range 1493.3-1458.4 cm^{-1} indicating the presence of N=N. The above observations are agreed with the assigned structures of compounds 4a-4d and other compounds (4e-4j). The Infra-red (Kbr) Spectrum of the newly synthesized compound (2-methoxy-5-methyl)phenyl malonamic acid[1a] shows absorption at 1594.0 cm^{-1} reveals -CONH, absorption at 3416.3 cm^{-1} indicates -NHstretching vibrations , absorption at 3007.4 cm^{-1} reveals the aromatic -CH, absorption at 1374.7 indicating -CH_2,absorption at 1718.1 indicates the presence of -COOH group . These observations are agreed with the assigned structure of the newly synthesized compound 1a. The IR (Kbr) Spectrum of N[I] -(2-methoxy-5-methyl) phenyl malonamide[5a] shows absorption at 1541.4 cm^{-1} reveals -C=C , absorption at 1649.8 cm^{-1} indicates -CONH , absorption at 3411.6 cm^{-1} reveals -NH , absorption at 2937.7 cm^{-1} indicating aromatic -CH stretching vibrations, absorption at 1325.4 cm^{-1} reveals the presence of -CH_2 .

Table 2: IR Asorption bands

Compound No.	Ar C=C Cm^{-1} stretching	HC=N Cm^{-1} stretching	-OH Cm^{-1} stretching	N=N Cm^{-1} stretching	CONH Cm^{-1} stretching	Lactone C=O Cm^{-1}	NH Cm^{-1} stretching	Ar CH Cm^{-1} stretching	CH_2 Cm^{-1} stretching	COOH Cm^{-1} stretching
1a	1562.8	-	-	-	1594.0	-	3416.3	3007.4	1374.7	1718.1
3a	1552.0	-	-	1491.1	1600.9	1717.4	3449.9	-	-	-
3b	1546.2	-	-	1491.7	1609.9	1730.5	3427.4	-	-	-
3c	1546.2	-	-	1492.0	1603.8	1716.9	3421.9	-	-	-
3d	1544.7	-	-	1493.4	1594.6	1715.1	3418.0	-	-	-
4a	1540.0	2364.3	3423.8	1465.4	-	-	-	-	-	-
4b	1539.1	2363.8	3418.0	1458.4	-	-	-	-	-	-
4c	1538.7	2360.1	3411.5	1462.0	-	-	-	-	-	-
4d	1541.8	2364.0	3424.2	1493.3	-	-	-	-	-	-
5a	1541.4	-	-	-	1649.8	-	3411.6	2937.7	1325.4	-

The above observations are lent support to the assigned structure of the compound 5a. The IR Spectra of all novel newly synthesized Azo-coumarins and Schiff's bases, substituted malonamide and substituted malon anilic acid indicating the absorption spectrum was in agreement with the assigned structures and their colouring properties . The Azo-coumarins were found to possess higher melting points and Schiff's bases were found to possess lower melting points, the azo-coumarins have more thermal stability as compaired to Schiff's bases.

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