IOSR Journal Of Pharmacy www.iosrphr.org
(e)-ISSN: 2250-3013, (p)-ISSN: 2319-4219
Volume 8, Issue 8 Version. I (August 2018), PP. 51-57

Synthesis & characterization studies of some derivatives of 1, 4-Naphthoquinone substituted C_1-NOH, C_2-NH_2, (N-acetyl) acetamido and C_3-Cl

Shubhangi V. Kulkarni, Raghunath G. Sarawadekar & Avinash B. Pawar
Department of Chemistry, Bharati Vidyapeeth (Deemed to be University), Yashwantrao Mohite College of Arts, Science & Commerce, Pune – 411038, INDIA.
Corresponding author: Shubhangi V. Kulkarni

ABSTRACT
The invention relates to a material for destructing micro algae with specific substituents. The compounds contain 1, 4 - Naphthoquinone as a basic one and substitution is carried out at C_1, C_2, and C_3 (C_1-NOH, C_2-NH_2 or (N-Acetyl) - acetamido and C_3-Cl). Amino Naphthoquinone can be embedded on cotton fabrics for good durability. Synthesis of 2-Amino-3-Chloro-1,4- Naphthoquinone (L_1), 2-(N-acetyl) – acetamido-3-Chloro-1,4 – Naphthoquinone(L_2), 2-Amino-3-Chloro-1,4-Naphthoquinone-1,Oxime(L_3)and2-(N-acetyl)–acetamido-3-Chloro-1,4Naphthoquinone-1,Oxime (L_4) were carried out. X-ray diffraction studies show that all these ligands are crystalline in nature and belongs to triclinic group. Crystalline parameters and h, k, l values are calculated by using McMallie computer code. The crystalline size is determined by Scherrer formula and found to be L_1-58.045 nm, L_2-48.314 nm, L_3- 64.97 nm and L_4- 49.54 nm. Infrared spectra shows characteristic frequencies for C-H, N-H, C=O, C=C and C-N. UV-VIS spectra shows electronic transition for $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$. The results are discussed in this paper.

Keywords - 2-Amino-3-Chloro-1, 4- Naphthoquinone, XRD, IR

Date of Submission: 02-08-2018 Date of acceptance: 17-08-2018

I. INTRODUCTION

Novel Naphthoquinones are reported and tested as inhibitors of M. Tuberculosis, methionine amino peptides variants and structure activity relationship (1). Naphthoquinonederivatives contain chloro and amino functional groups are useful for prevention of amyloid deposit and decreases involving amyloid genesis (2). 2-Amino-3-Chloro-1, 4-Naphthoquinone was amidated by acetic anhydride and data for biological activity was reported (3). This compound is used for processing regions with green algae or red algae to prevent green algae or red algae (4). It is also reported as hNAT1 inhibitors useful in treatment of breast cancer (5). It is reported that such compound used in batteries in electrolyte solutions and it improves the safety of battery (6). This ligand is used as inhibitors of MITF pathways, MITF inhibitors are further used for treatment of cancer (7). It can be used for the preparation of vitamin K analog as antiproliferative agent and testing for biological activity (8). Naphthoquinone derivatives of 1,4- Naphthoquinone with substitution as Cl, NH_2 can be used as agent especially effective on fishnets for a long period (9). The chloro group of 2-acetamido-3-chloro-1, 4-Naphthoquinone play an important role in the antiplatelet activity in addition to the amide linkage (10). The IR and spectral properties of 2-amino-3chloro-1, 4-Naphthoquinone were reported and it belongs to 2-azido-3chloro-1,4-Naphthoquinone (11). We have synthesized 2-amino-3-chloro-1,4-Naphthoquinone,2-(N-acetyl)-acetamido-3-chloro-1,4-Naphthoquinone, 2-amino-3-chloro-1,4-Naphthoquinone-1-oxime,2-(N-acetyl) acetamido-3-chloro-1,4-Naphthoquinone-1-oxime and their characterization is carried out by X-ray diffraction, Infra-red spectroscopy and UV-Visible spectroscopy. The results are discussed in this paper.

II. MATERIALS & METHODS

Synthesis of 2-amino-3chloro-1,4-Naphthoquinone was carried out as per the procedure given by Mastura Makoto et.al.(12). The reaction between methyl amine in methanol with 2.3-dichloride-1, 4-Naphthoquinone carried out over 2 hours at $30\text{-}40^0$ C and yield was 96.6%. Synthesis of 2-(N-acetyl) acetamido-3-chloro-1, 4-Naphthoquinone was carried out as per the procedure given by Ngoc-Chau Tran et.al. (13). 2-amino-3-chloro-1,4-Naphthoquinone-1-oxime and 2-(N-acetyl) acetamido-3-chloro-1,4-Naphthoquinone-1-oxime were carried out as per reported method (14).

2.1 Instrumental analysis

C,H & N analysis was carried out on ThermoFinnigan instrument. X-ray diffraction pattern were obtained on Rigaku Model 4, Miniflex using CuK-α (1.5404A^0) radiations at room temperature. IR Spectra were recorded on a JASCO FTIR Spectrophotometer model in a KBr matrix and in the range of 4000-400 cm^{-1} . UV-VIS spectra were recorded on JASCO 530 model in DMSO in the range of 200-800 nm at room temperature.

III. RESULTS AND DISCUSSION

3.1X-Ray Diffraction

Fig1 shows x-ray diffraction patterns of L_1, L_2, L_3 &L_4

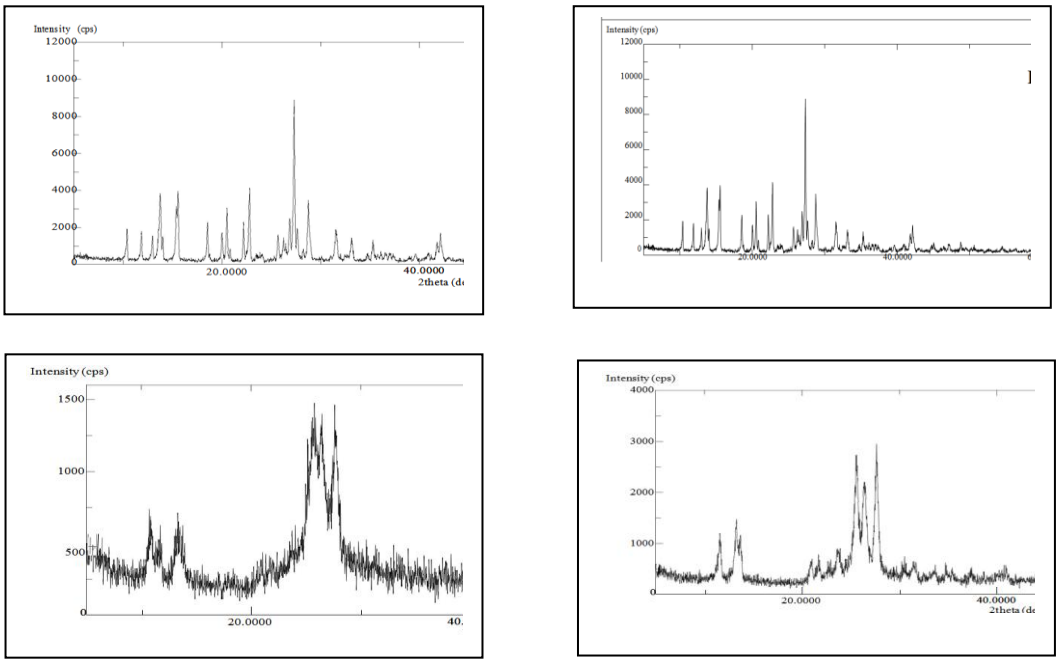


Fig1: x-ray diffraction patterns of L_1, L_2,L_3 & L_4

X-Ray Diffraction data such as d-value and intensity ratios of L_1, L_2, and L3&L_4 are given in Table No1.

Table No. 1: d-value and intensity ratios of L1, L_2, L_3 &L_4.

Sr.	L_1		L_2		L_3		L_4	
No.	d-value	I/Io	d-value	I/Io	d-value	I/Io	d-value	I/Io
1	8.52	19	10.32	6	8.11	27	7.62	30
2	7.46	17	10.23	6	6.76	19	6.67	47
3	6.83	13	10.20	6	6.59	27	6.47	34
4	6.44	40	10.06	4	4.23	16	4.23	15
5	6.32	14	10.02	7	4.09	16	4.10	18
6	5.76	33	9.84	7	4.03	16	4.06	12
7	5.70	42	9.80	7	3.78	20	3.87	14
8	4.78	22	5.74	4	3.74	26	3.77	25
9	4.44	17	5.73	4	3.70	24	3.72	21
10	4.32	33	5.70	5	3.61	32	3.68	11
11	4.00	25	5.66	12	3.54	67	3.64	17
12	3.90	41	5.65	4	3.48	94	3.60	17
13	3.47	17	5.62	6	3.45	96	3.57	24
14	3.39	14	5.21	8	3.37	100	3.53	36
15	3.37	10	5.15	4	3.28	54	3.50	74
16	3.31	26	5.10	5	3.23	88	3.48	100

17	3.26	100	5.09	5	3.22	100	3.37	76
18	3.23	21	5.06	5	3.20	85	3.34	48
19	3.10	38	5.02	5	3.14	29	3.30	24
20	3.09	13	5.00	4	3.09	24	3.22	100
21	2.83	19	4.98	4	3.07	21	3.17	16
22	2.82	11	4.01	4	3.04	19	3.13	11
23	2.70	14	4.00	4	3.00	21	3.11	10
24	2.54	12	3.99	5	2.93	19	3.08	9
25	2.16	12	3.98	6	2.87	16	3.04	10

The crystal structure of Zinc Lawsonate & Lead Lawsonate belongs to triclinic group and the data is given by A. B. Pawar et.al. (15). The crystal structure of Zinc Juglonate & Lead Juglonate belongs to triclinic group and the data is given by A B Pawar et.al. (16). The crystal structure of Lawsone Monoxime, Zinc Lawsone Monoxime and Lead Lawsone Monoxime also belongs to triclinic group (17). It is observed that all the ligands are crystalline in nature, the data was processed by using McMaille computer program (18) for determination of cell parameters. L1 crystallizes in the triclinic group and it has crystallographic parameters such as: a = 9.2610 A^0,b = 7.2229 A^0 and c = 14.2307 A^0, $\alpha = 72.573^0$, $\beta = 73.549^0$, and $\lambda = 108.252^0$. Its volume is 784.311 (A^0) and its minimum density is Dmin = 3.363302 g/cm^3. Calculated and measured h, k, l data is given in Table No 2

Table No 2: data for h, k, l value of L_1

h	k	l	TH(OBS)	TH(ZERO)	TH(CALC)	DIFF	d
1	0	1	10.380	10.377	10.370	0.007	8.5153
0	1	1	12.960	12.957	12.940	0.017	6.8253
1	-1	0	13.740	13.737	13.727	0.009	6.4396
1	0	2	14.000	13.997	13.995	0.001	6.3205
0	1	-1	18.540	18.537	18.522	0.015	4.7818
2	-1	0	20.520	20.517	20.514	0.003	4.4359
2	0	0	22.200	22.197	22.210	-0.013	4.3246
2	-1	-1	22.760	22.757	22.779	-0.022	3.9038
1	-2	-2	25.660	25.657	25.648	0.009	3.4688
1	0	4	26.240	26.237	26.245	-0.008	3.3934
0	2	1	26.440	26.437	26.444	-0.007	3.3682
1	-1	3	26.880	26.877	26.902	-0.025	3.3141
2	1	2	27.300	27.297	27.295	0.002	3.2640
0	2	3	27.620	27.617	27.637	-0.020	3.2269

L_2 crystallizes in the triclinic group and it has crystallographic parameters such as:
a = 11.8514 A^0,b = 5.9405 A^0 and c = 11.6171 A^0
$\alpha = 77.572^0$, $\beta = 66.047^0$, and $\lambda = 105.553^0$
Its volume is 669.517 (A^0) and its minimum density is Dmin = 5.125219 g/cm^3. Calculated and measured h, k, l data is given in table no 3

Table No 3: data for h, k, l value of L_2

h	k	l	TH(OBS)	TH(ZERO)	TH(CALC)	DIFF	d
0	0	1	8.980	8.949	8.951	-0.002	9.8394
1	0	1	9.020	8.989	8.986	0.003	9.7959
1	-1	0	15.460	15.429	15.431	-0.002	5.7268
2	0	1	15.540	15.509	15.510	-0.001	5.6975
1	0	2	15.640	15.609	15.609	0.000	5.6613
0	1	0	16.680	16.649	16.647	0.002	5.6469
0	1	1	15.760	15.729	15.731	-0.002	5.6184
1	-1	-1	17.000	16.969	16.967	0.003	5.2113

L_3 crystallizes in the triclinic group and it has crystallographic parameters such as:
a = 12.7628 A^0,b = 8.8124 A^0 and c = 13.5800 A^0
$\alpha = 103.421^0$, $\beta = 86.774^0$, and $\lambda = 87.152^0$
Its volume is 1480.181 (A^0) and its minimum density is Dmin = 3.184194 g/cm^3. Calculated and measured h, k, l data is given in Table No 4

Table No 4: data for h, k, l value of L_3

h	k	l	TH(OBS)	TH(ZERO)	TH(CALC)	DIFF	d
0	1	-1	10.900	10.902	10.916	-0.014	8.1102
1	-1	1	13.080	13.082	13.057	0.025	6.7630
0	0	2	13.420	13.422	13.428	-0.006	6.5924
1	-2	1	21.700	21.702	21.714	-0.012	4.0920
3	1	-1	23.500	23.502	23.491	0.011	3.7825
2	0	3	23.780	23.782	23.785	-0.003	3.7386
3	-1	0	24.000	24.002	24.006	-0.004	3.7048
2	-2	1	25.160	25.162	25.151	0.011	3.5366
3	-1	2	25.560	25.562	25.576	-0.014	3.4822
2	2	-2	25.840	25.842	25.847	-0.005	3.4451
1	-1	-3	26.400	26.402	26.404	-0.002	3.3732
1	-1	4	27.200	27.202	27.192	0.010	3.2758
1	2	2	27.700	27.702	27.698	0.004	3.2178
1	1	-4	27.820	27.822	27.824	-0.002	3.2042

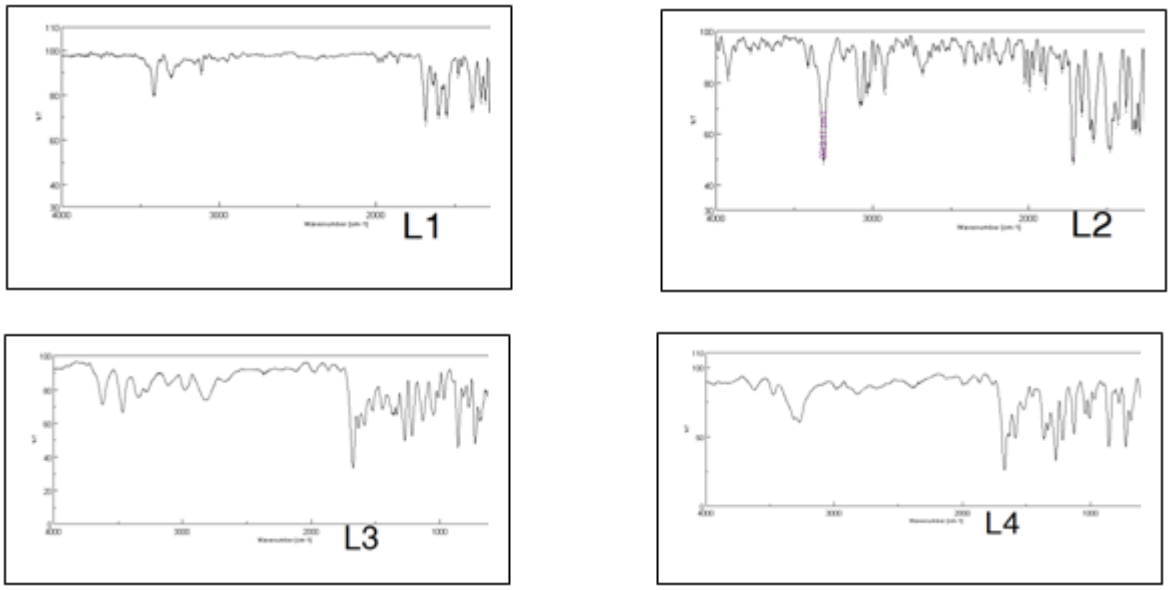
L_4 crystallizes in the triclinic group and it has crystallographic parameters such as:
a = 10.9057 A^0,b = 7.5941 A^0 and c = 8.5696 A^0
$\alpha = 107.096^0$, $\beta = 73.044^0$, and $\lambda = 79.746^0$
Its volume is 621.288 (A^0) and its minimum density is Dmin = 2.961961 g/cm^3. Calculated and measured h, k, l data is given in Table No 5

Table No 5: data for h, k, l value of L_4

h	k	l	TH(OBS)	TH(ZERO)	TH(CALC)	DIFF	d
0	0	1	11.600	11.605	11.598	0.008	7.6223
1	1	0	13.260	13.265	13.244	0.021	6.6716
0	1	-1	13.680	13.685	13.717	-0.032	6.4677
2	1	1	21.000	21.005	21.012	-0.007	4.2268
1	0	2	21.680	21.685	21.684	0.001	4.0958
2	1	-1	22.960	22.965	22.952	0.013	3.8703
2	0	2	23.600	23.605	23.602	0.003	3.7667
0	2	-1	23.900	23.905	23.902	0.003	3.7201
2	-1	0	24.740	24.745	24.751	-0.006	3.5957
3	0	1	24.940	24.945	24.943	0.003	3.5673
2	-1	2	25.180	25.185	25.180	0.006	3.5338
1	1	-2	25.580	25.585	25.596	-0.011	3.4795
3	1	1	26.440	26.445	26.454	-0.009	3.3682
2	2	0	26.660	26.665	26.670	-0.004	3.3409
0	2	-2	27.640	27.645	27.637	0.009	3.2247
1	1	2	28.160	28.165	28.162	0.003	3.1663
2	1	2	28.520	28.525	28.527	-0.002	3.1271

3.2 Infrared spectroscopy

Fig2 shows IR frequencies of L_1,L_2,L_3& L_4



IR Spectra and frequencies of 2-amino-3-chloro-1,4,Napthoquinone is reported by S V Kulkarni et.al. The vibrational wave numbers of this compound have been calculated using Gaussian software code, employing density functional theory. The IR data was compared with experimental values. The predicted infrared intensities and Raman activities were reported (19). The IR spectra of L_1, L_2, L_3&L_4 were determine in KBr matrix. The data for different stretching & bending vibrations of these compounds are reported for N-H, C-H, C=O, C-N, C=N, N-O and O-H. All the frequencies are compared to the literature values. The frequencies of C=O, N-O, C=N matching to the reported values (17). The frequencies of C-N, O-H & C-Cl are matching to the reported values (19). The data of IR frequencies ofL_1, L_2, L_3&L_4 is given in Table No 6.

Table No 6: IR bands of L_1, L_2, L_3 & L_4

Sr. No	Comp.	N-H	C-H	C=O	C-N	O-H	C=N	N-O	C-CL
1.	L1	3414	3112	1639	1686	-	-	-	594
2.	L2	3412	3080	1587	1683	-	-	-	592
3.	L3	3463	3108	1632	1672	3621	1521	1130	478
4.	L4	3472	3268	1671	1671	3624	1522	1129	533

3.3Electronic Spectra:

Fig3 shows UV bands of L_1, L_2, L_3&L_4in nm

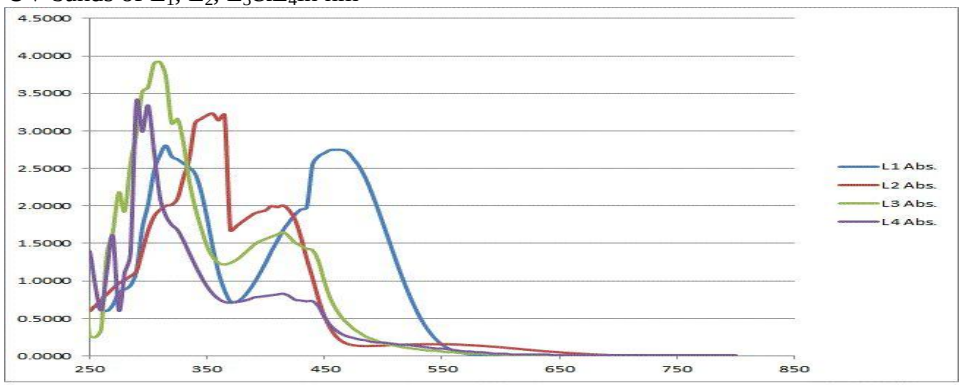


Fig 3: UV bands of L_1, L_2, L_3&L_4

The electronic transition of L_1, L_2, L_3 & L_4 are given in Table No 7.

Table No.7 : Electronic spectra of ligand L_1, L_2, L_3 & L_4 in DMSO:

Compound	**ƛ max$_1$nm** **a)** $\pi \rightarrow \pi^*$	**ƛ max$_2$nm** **b)** $\pi \rightarrow \pi^*$	**ƛ max$_3$nm** **c)** $n \rightarrow \pi^*$
L1	245	315	460
L2	---	355	415
L3	286	362	413
L4	247	298	412

a) Benzenoid transition
b) Quinonoid transition
c) Charged transition.

The ultraviolet visible spectrum is determined in DMSO solvent. L_1 spectrum shows 3 peaks at 245 nm, 315 nm & 460 nm. First peak is assigned as $\pi \rightarrow \pi^*$ which is also known as Benzenoide electronic transition. Second pick is $\pi \rightarrow \pi^*$ which is generally assigned as Quinonoid electronic transition. Third peak is due to $n \rightarrow \pi^*$ which is also known as charged transition. L_2 ligand shows only 2 peaks, first at 355 nm and second at 415 nm. We do not observe Benzenoide transition but first peak is due to quinonoid transition. The peak is at 415 nm is due to $n \rightarrow \pi^*$. It is associated with the intramolecular ligands charged resonance (20). Ligand L_3 gives 3 bands at 286 nm, 362 nm & 413 nm and the assignments are similar to ligand L1. Ligand L_4 gives 3 bands at 27 nm, 298 nm & 412 nm. First band is due to Benzene electronic transition i.e. $\pi \rightarrow \pi^*$. The second peak is for QET which is due to $\pi \rightarrow \pi^*$ transition and third band of $n \rightarrow \pi^*$ transition show bathochromic effect at 412 nm (21).

IV. CONCLUSIONS

All the ligands are crystalline in nature and belong to triclinic group. The infrared spectra compared with reported values and show good relation between them. Electronic spectra shows the bands to $\pi \rightarrow \pi^*$ & $n \rightarrow \pi^*$, which are closely matched to the reported work.

ACKNOWLEDGMENTS

We thank to the Principal, Bharati Vidyapeeth (Deemed to be University), Yashwantrao Mohite College of Arts, Science & Commerce, Pune for permission to publish this work.

REFERENCES

[1]. Liu, Jun O,: Oaleye, OmonikeArike: Bhat, Shridhar, "Preparation of Naphthoquinone and Naphthothiazole compounds as therapeutic inhibitors of methionine amino peptidases", PCT Int. Appl. WO 2011017519 A2 20110210(2011).

[2]. Scherzer, Roni: Gazit, Ehud: Segal, Daniel,"Naphthoquinone derivatives useful for prevention of amyloid deposits and treatment of diseases involving amyloid genesis", PCT Int. Appl. WO 2010026592 A1 20100311 (2010),.

[3]. Lee, KuoHsiung: Kuo, Sheng-Chu: ibuka, Toshiro, "Preparation of naphtha(2,3-d) imidazole-4,9-diones and analogs as antitumor agents", PCT Int. Appl. WO 9730022 A1 19970821(1997),.

[4]. Cho, Hun:, "Composition containing Naphthoquinone for controlling microalgae",Repub, Korian Kongkae Taeho Kongbo KR 2014105423 A 20140901(2014),.

[5]. Russell, Angela Jane:Sim, Edith: Daviess, Steven Graham: Westowood, Isaac Mark: Kawamura, Akane: Crawfprd Matthew Howard James: Laurieri, Nicola, "Preparation of Naphthoquinone derivatives for us as hNAT1 inhibitors useful in treatment of breast cancer", PCT Int. Appl. WO 2011055142 A2 20110512 (2011),.

[6]. Maejima, Toshikazu, "Secondary lithium batteries using electrolyte solutions containing Quinone additives", PCT Int. Appl. WO 10021958 A 19980123 (1998),.

[7]. Falon Patrick: Weiner, Warren S: Smith, Robert A, Schoenen, Frank John: David E: Hag Rizwan "Preparation of substituted aminonapthalenediones as inhibitors of MITF molecular pathways" PCT Int. Appl. WO 2014201016 A2 20141218 (2014),

[8]. Carr, Brian I: Wilcox, Craig S: Kerns, Jeffery K. "Preparation of vitamin K analogs as antiproliferative agents" PCT Int. Appl.WO 2000008495 A2 20000217. (2000),

[9]. Suetake, Yeukio, Kadota, Osamu "Antifouling compositions containing 1,4 Naphthoquinones" Jpn, Kokai, TokkyoKoho, JP 01175903 A 19890712 (1989)

[10]. Jin-Cherng Lien, Li-Jiau Huang, Jih-Pyang Wang, Che-Ming Teng, Kuo-Hsiung Lee and Sheng-ChuKuo "Synthesis and Antiplatelet, Antiinflammatory and AntiallergicActivites of 2,3-Disubstituted 1,4-Naphthoquinones" Chem. Pharma. Bull.44 (6) 1181-1187 (1996)
[11]. J.A.Van Allen, W.J.Priest, A.S.Marshall, G.A.Reynolds "The thermal and photolytical decomposition of 2-3-diazido-1,4-Naphthoquinone and certain related Azidoquinones" The journal of organic Chem. 33, 1100 (1968).
[12]. Matsura, Makato: Yamada, Yoninogu: Sakai, Kazuki: Bando, Kazo and Sato, Joben, TokkyoKoho JP 53031651 A 19780325 (1978).
[13]. Ngoc-Chau Tran, Minh-Tri-Le, Dinh-Nga Nguyen, Jhanh-Dao Tran: "Synthesis and Biological evaluation of halogen substituted 1,4-Naphthoquinone as potent antifungal agents" 13th International electronic conference on synthetic organic chemistry (ECSOC-13), 1-13 November 2009.
[14]. Jagtap S.B., Joshi S..J., Litke G.M., Ghole V.S. and Kulkarni B.A., "Metal based drugs , 7 (3) 147-150 (2001).
[15]. A.B. Pawar, A.A. Killedar, K.D. Jadhav and R. G. Sarawadekar, "X-ray diffraction, Spectral and antimicrobial activity of bivalent metal (Zn, Cd, Hg, Pb and Sn) chelates of 2-hydroxy-1,4-Napthoquinone" International journal of Chemtech research Vol. 4 No.3, PP 882-890 (2012).
[16]. A. B. Pawar, S. R.Bamne, K. D. Jadhav and R. G. Sarawadekar, "Spectral, Thermal, X-ray diffraction and antimicrobial activity of bivalent metal (Zn, Cd, Hg, Pb and Sn) chelates of Juglone" J. Curr. Chem. Pharm. Sc.: 2 (4), 277-290, (2012).
[17]. A. B. Pawar, R. G. Sarawadekar, K. D. Jadhav and S. S. Kadam, "Thermal, X-ray diffraction, Spectral and antimicrobial activity of bivalent metal (Zn, Cd, Hg, Pb and Sn) chelates of 2-hydroxy-1,4-Napthoquinone-1,Oxime" IOSR Journal of pharmacy and biological services, Vol 3, Issue 3, PP 01-08 (2012).
[18]. A. Le Bail, Powder Diffraction, 19, 249-259 (2004).
[19]. Shubhangi V. Kulkarni, Raghunath G.Sarawadekar & Avinash B. Pawar "Synthesis and vibrational study of 2-amino-3-chloro,1-4-Naphthoquinone by DFT" International journal of chemtech Research 10(15) (2017)
[20]. Silverstein R. M., Bassler G. C. and Morrill T. C. "Spectrometric Identification of organic compounds" 4thed New York: John Wiley and sons 1981.
[21]. A. B. Pawar, S. R.Bamne, K. D. Jadhav and R. G. Sarawadekar, "Spectral, Thermal, X-ray diffraction and antimicrobial studies of some bivalent metal chelates of Juglone", J. Curr. Chem, Pharm sci : 2(4), 277-299 (2012).

Shubhangi V. Kulkarni, Synthesis & characterization studies of some derivatives of 1, 4-Naphthoquinone substituted C1-NOH, C2-NH2, (N-acetyl) acetamido and C3-Cl." IOSR Journal of Pharmacy (IOSRPHR), vol. 8, no. 8, 2018, pp. 51-57..