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Aminothienochromene based Bisazo Disperse Dyes: Synthesis, Characterization and Dyeing Application

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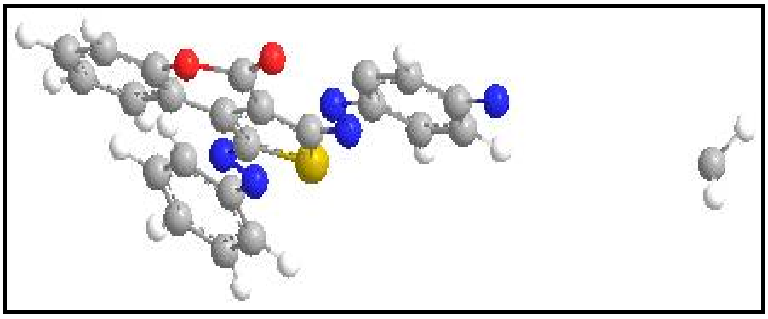
ABSTRACT

A series of novel bisazo disperse dyes have been synthesized via an easy and efficient methodology. In the present investigation we have synthesized monoazo dyes by the reaction of 3-Amino-4H-thieno[3,4-c]chromen-4-one with various substituted 3^o amine coupling components. These monoazo dyes were then coupled with various diazotized primary amines to yield bisazo dyes. The chemical structure of the synthesized dyes was investigated using FTIR, ^{1}H NMR, elemental analysis and UV spectroscopy. All the synthesized compounds were studied and their dyeing performance was evaluated. The synthesized dyes were applied to polyester fabrics by using high temperature dyeing method at 130°C. The results of fastness properties of the dyes on polyester fabric gave excellent sublimation ratings, excellent washing fastness, perspiration ratings and good light fastness ratings.

Graphical Abstract



Keywords: Bisazo disperse dyes, 3-Amino-4*H*-thieno[3,4-c]chromen-4-one, Tertiary amines, Primary amines and Dyeing performance.

INTRODUCTION

Azo dyes represent 60-80% of all organic colorants, the single largest chemical class of industrial colorants which are synthesized through azo coupling between a diazonium compound and another aromatic compound [1-6]. They are used as light absorbance for plastics and as substrates for many industrial applications such as textile fibers, leather, paper, hair, mineral oils, waxes, foodstuffs and cosmetics [7]. The use of heterocyclic intermediates [8] in the synthesis of azo dyes is well established and the resultant dyes exhibit good tinctorial strength. In recent times, focus has been shifted to incorporating of azomoiety into heterocycle systems. The heterocyclic moiety may involve as the first component, middle component as well as end component of bisazo disperse dyes.

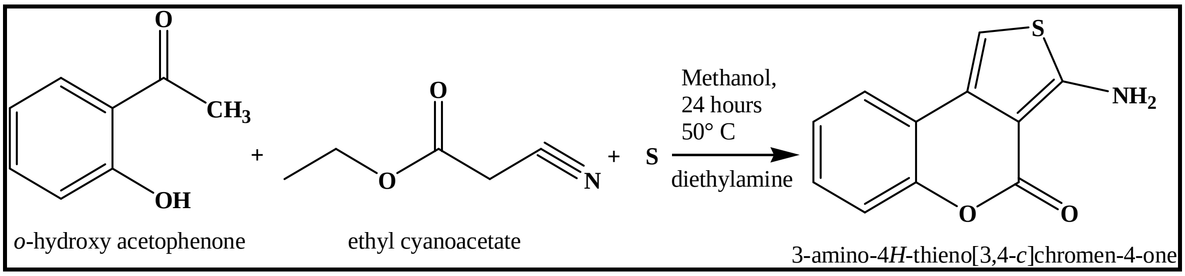
In disperse dye chemistry a number of heterocycles have been used as heteroaromatic diazo or coupling components [9, 10]. Disperse dyes [11, 12] emerge as a fairly common class of dyes for application to the majority of synthetic fibers. Coumarin derivatives play an important role in organic synthesis [13, 14]. Coumarins are also used as fluorescent brighteners, efficient laser dyes and additives in food and Cosmetics [15]. While coumarin is a colourless compound, some of its derivatives exhibit colour and intense fluorescence. They have applications in pharmaceuticals, optical brighteners [16, 17] and laser dyes [18]. Chromene based dyes have high degree of brightness compared with azo dyes derived from anilines [19] and also excellent brightness of shades.

Reported that synthesis of the dyes, which are prepared by diazotization of 3-Amino-4*H*-thieno[3,4-c]chromen-4-one and then coupled with various 3^o amine coupling component and gives monoazo dyes which on further coupled with diazotized primary amines and gives bisazo dyes.

MATERIALS AND METHODS

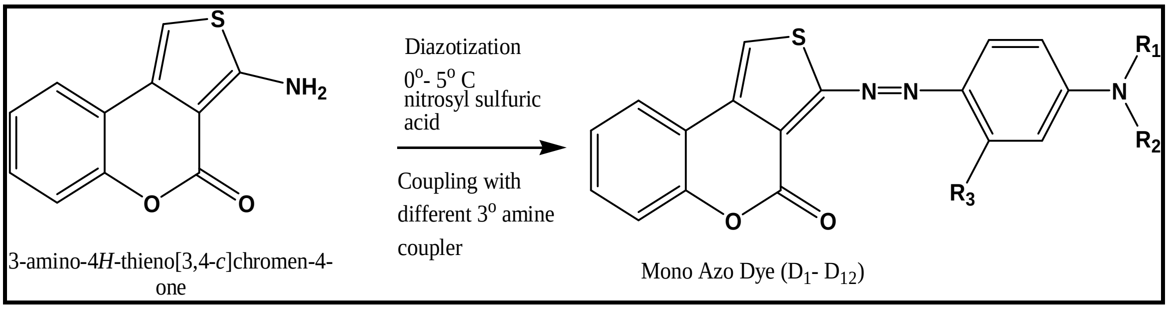
All the chemicals used were of analytical reagent grade and were used without further purification. Melting points were taken in open capillary on Stuart SMP 10 melting point apparatus and are uncorrected. The purity of all compounds was determined by thin-layer chromatography (TLC) using silica gel-G coated Al-plates (0.5 mm thickness, Merck) and spots were visualized under UV radiation. IR spectra were recorded on Perkin-Elmer 1600 FTIR in KBr pellets. ^{1}H NMR spectra were taken on a Bruker Avance II 400 NMR MHz in DMSO as solvent and TMS as internal standard and elemental analysis of “Nitrogen” was carried on Carlo Erba 1108 instrument at SAIF Central Instrumentation Laboratory, Panjab University, Chandigarh. Absorption spectra of the dyes were recorded on a Shimadzu UV-1800 spectrophotometer in DMF.

Step-1: Synthesis of 3-Amino-4*H*-thieno[3,4-c]chromen-4-one (S_1): A mixture of *o*-hydroxy acetophenone (27.2 g, 0.2 mol), sulphur (6.4 g, 0.2 mol) and ethyl cyano acetate (22.6 g, 0.2 mol) respectively in methanol (200 mL) was stirred using a magnetic plate stirrer for 24 h at 50°C in the presence of diethylamine as base catalytic amount. Completion of the reactions was monitored by TLC. The solid that formed was collected by using filtration and crystallized from benzene to give compound $\mathbf{S_1}$as a yellow powder, Yield 48%, m.p.197°-199°C. Anal. Calcd. for $C_{12}H_9NOS$; N, 6.51, Found: N, 6.36.

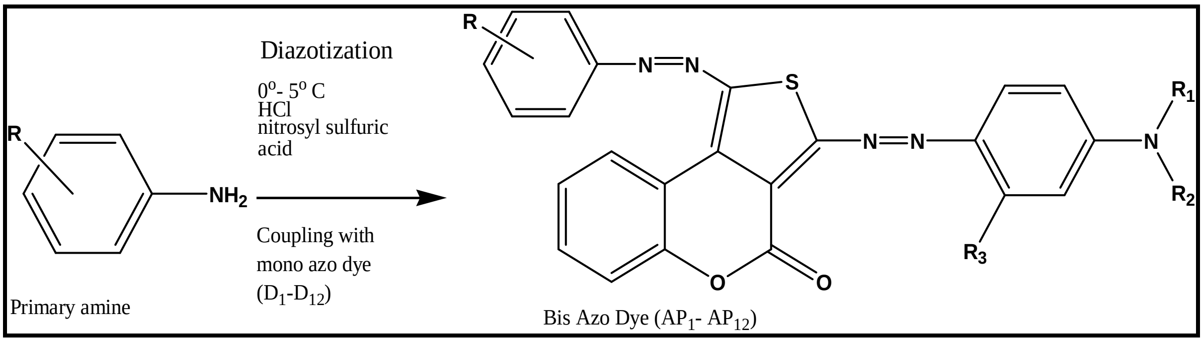


Step-2: Diazotization of 3-Amino-4*H*-thieno[3,4-c]chromen-4-one: Compound $\mathbf{S_1}$ (2 g, 0.009 mol) was dissolved in mixture of acetic acid and sulphuric acid (13.0 + 5.0 mL) and cooled to 0°-5°C. Dry sodium nitrite (0.621 g, 0.009 mol) was slowly added over a period of 30 min to concentrated sulphuric acid (3 mL) and heated up to 60°C till all solid dissolved and then rapidly cooled at 0°-5°C. The solution was cooled to 0°-5°C. The nitrosyl sulphuric acid solution was added to the solution of $\mathbf{S_1}$ and the temperature was maintained to 0°-5°C. Stirring was continued, maintaining the same temperature for an hour, with positive test for nitrous acid on starch iodide paper, excess of nitrous acid was removed by adding required amount of sulphamic acid. This clear diazonium salt solution was used immediately in the coupling reactions.

Step-3: Coupling of diazotized solution with different substituted 3° amines coupling component: Formation of mono azo dyes (D_1-D_{12}): Substituted 3° amines (0.009 mol) coupling component was dissolved in acetic acid solution (6.0 mL). The solution was cooled to 0°-5°C in an ice-bath. To this well-stirred solution, the above diazonium solution was added dropwise keeping the temperature below 5°C. The reaction mass was further stirred for 2 h at 0°-5°C maintaining the pH at 5.5 to 6.0 by adding the required amount of 20% sodium acetate solution. The dye was isolated by filtration, washed with cold water, dried and powdered.



Step-4: Formation of bis azo dyes (AP_1-AP_{12}): The solution of *p*-chloro *o*-nitro aniline (1.72 gm, 0.01 mole) in 5mL hydrochloric acid was stirred at 0°-5°C. Dry sodium nitrite (0.69 g, 0.01 mol) was slowly added over a period of 30 min to concentrated sulphuric acid (3 mL) and heated up to 60°C till all solid dissolved and then rapidly cooled at 0°-5°C. The solution was cooled to 0°-5°C. The nitrosyl sulphuric acid solution was added to the solution of $\mathbf{S_1}$ and the temperature was maintained to 0°-5°C. Stirring was continued, maintaining the same temperature for an hour, with positive test for nitrous acid on starch iodide paper, excess of nitrous acid was removed by adding required amount of sulphamic acid. This clear diazonium salt solution was used immediately in the coupling reactions. 3-((4-(diethylamino)phenyl)diazenyl)-4*H*-thieno[3,4-c]chromen-4-one (3.77 g, 0.01 mol) was dissolved in mixture of acetic acid and sulphuric acid (15.0 + 5.0 mL) and cooled to 0°-5°C. The diazonium salt of *p*-chloro *o*-nitro aniline was added dropwise at the same temperature and maintaining pH 5.5 to 6.0 by adding solution of 20% w/v sodium acetate. The resulting reaction mixture was stirred for 3h at 0°-5°C. The resultant dye was filtered off and washed with cold water and dried. The colored dye $\mathbf{AP_1}$ was filtered off, dried at 60°-70°C and recrystallized from acetone. Remaining Dyes **(AP_2-AP_{12})** were synthesized by same method by using different primary amine instead of *p*-chloro *o*-nitro aniline.



RESULTS AND DISCUSSION

Chemistry: *o*-hydroxyacetophenone reacted with elemental sulphur and ethyl cyano acetate in methanol in the presence of diethylamine as catalytic amine base gives 3-Amino-4*H*-thieno [3,4-c]chromen-4-one **(S_1)** by cyclization. Diazotization of compound **(S_1)** was carried out and the resulting diazonium salt solution was coupled with various substituted 3° amine coupling components gave mono azo dyes **D_1 -D_{12}**. This mono azo dye was then coupled with diazotized primary amines and gave final dyes **AP_1–AP_{12}**. The new compounds were confirmed by elemental analysis, IR, ^1H NMR and UV spectral data.

Visible absorption spectroscopic properties of dyes: The visible absorption spectra of dyes were performed in DMF and are shown in table 1. Their absorption maxima were in the range of 382.5-579 nm. The color of the dyes is affected by the substituent in the coupler and diazonium salt molecule. It is due to the oscillation of electrons and the presence of additional substituents. The introduction of electron-donating groups $-CH_3$, $-C_2H_5$, $-NHCOCH_3$, $-OCOCH_3$, $-OCH_3$ and -OH or electron-withdrawing groups -CN, -Cl, -Br and $-NO_2$ at respective positions in the coupling components as well as diazonium components affect the absorption characteristics of the dyes. It is clear that the value of λ_{max} depends on the electron-donor or electron-acceptor nature and colour change observed for each dye is due to the alternation of electrons and the presence of additional substituent.

IR spectra: IR Spectra of **S_1**showed a characteristic band at 3396.76 cm^{-1} for asymmetric and 3163 cm^{-1} for symmetric stretching is due to the $–NH_2$ group, stretching for –C=O group showed at 1680 cm^{-1} and 759.98 cm^{-1} is due to -C-S-C group.

The IR spectra of the dye **AP_2** showed the stretching vibration of alkyl group appeared at 3093.92 cm^{-1}, stretching for -C=O group showed at 1649.19 cm^{-1}, stretching vibration of -C=N group appeared at 1539.25 cm^{-1}. The azo group stretching vibration band appeared at 1467.67 cm^{-1} vibration band of $-NO_2$ group appeared at 1274.99 cm^{-1}, *p*-substituted benzene ring showed stretching vibration at 833.28 cm^{-1}, 759.98 cm^{-1} is due to -C-S-C group and vibration peak of the chlorine appearing at 663.53 cm^{-1}. The IR spectra of the dye **AP_3** showed the stretching vibration of alkyl group appeared at 3107.43 cm^{-1} , stretching for -C=O group showed at 1639.55 cm^{-1}, stretching vibration of -C=N group appeared at 1593.25 cm^{-1}, The azo group stretching vibration band appeared at 1471.74 cm^{-1}, vibration band of $-NO_2$ group appeared at 1276.92 cm^{-1}, *p*-substituted benzene ring showed stretching vibration at 831.35 cm^{-1} and 748.4 cm^{-1} is due to -C-S-C group.

^1H NMR spectra: ^1H NMR spectra of **S_1**exhibited singlet in the region at δ 8.16 ppm for two protons of $–NH_2$ and multiplets of five proton of aromatic ring resonates at δ 7.30 -6.27 ppm. ^1H NMR spectra of dye **AP_2** exhibited multiplets of eleven protons of aromatic ring in the region at δ 7.78 -6.70 ppm and singlet in the region at δ 3.37 ppm for six protons of $-N(CH_3)_2$ group. ^1H NMR spectra of dye **AP_3** one proton present in -NH group found to resonate as singlet at δ 10.36 ppm, multiplets of nine protons of aromatic ring in the region at δ 7.57 -7.12 ppm, four protons of $-N(CH_2)_2$ group is found as quartet at δ 3.53 -3.48 ppm, three protons of $–NHCOCH_3$ group found as singlet at δ 2.26 ppm and six protons of $(C-CH_3)_2$ is found as triplet at δ 1.24-1.13 ppm, the protons of $–CH_3$of $-NHCOCH_3$ group lies at higher δ value, because of deshielding effect of -C=O.

APPLICATION

Dyeing of fabric: According to usual procedure, all the dyes were applied on polyester fabrics in 2% shade, pH was adjusted 7.0 using soda ash solution during HTHP dyeing method. The colour for each dye was varying i.e. tortilla, olive, pearl grey, blood red, peanut, palm, oyster, dijon, egg nog and candy colors. The variation in the hues of the dyed fabric results from both the nature and position of the substituent present in the coupling components. The degree of levelness after washing indicates good dispersion and affinity of these dyes to the fabric.

Fastness properties of dyed fabric: The fastness ratings are shown in table 2. The light fastness properties were assessed in accordance with BS: 1006-1378 and the wash fastness test in accordance with IS: 765-1979. The light fastness of all the dyes exhibited the rating 3-5 for polyester which showed that light fastness was fair to good. The wash fastness of all the dyes had the rating 4-5 for

Table 1. The characterization data of dyes

Dye No.	Substituent				λmax (nm)	M.W.	Melting point (°C)	Yield %	Nitrogen	
	R_1	R_2	R_3	R					Found	Calc.
AP_1	$-C_2H_5$	$-C_2H_5$	-H	2-cyno 4-nitro 6-bromo aniline	579	630	123-125	74	15.60	15.55
AP_2	$-CH_3$	$-CH_3$	-H	4-chloro 2-nitro aniline	442.5	532	195-197	80	15.72	15.77
AP_3	$-C_2H_5$	$-C_2H_5$	$-NHCOCH_3$	2-cyno 4-nitro 6-bromo aniline	395.5	687	115-117	69	16.34	16.30
AP_4	$-C_2H_4CN$	$-C_2H_4CN$	-H	4-chloro 2-nitro aniline	477	611	132-136	72	18.36	18.34
AP_5	$-C_2H_4OH$	$-C_2H_4OH$	-Cl	4-chloro 2-nitro aniline	510	627	120-124	62	13.37	13.39
AP_6	$-C_2H_4CN$	$-C_2H_4OH$	$-NHCOCH_3$	Aniline	450.5	579	118-120	70	16.90	16.92
AP_7	$-C_2H_4CN$	$-C_2H_4CN$	$-CH_3$	4-chloro 2-nitro aniline	463.5	625	143-145	74	17.91	17.93
AP_8	$-C_2H_4OCOCH_3$	$-C_2H_4OCOCH_3$	-Cl	Aniline	541.5	632	98-100	71	11.06	11.08
AP_9	$-C_2H_4CN$	$-C_2H_4OCOCH_3$	$-NHCOCH_3$	Aniline	429.5	621	107-109	75	15.74	15.77
AP_{10}	$-C_2H_4CN$	$-C_2H_5$	-H	2-cyno 4-nitro 6-bromo aniline	382.5	655	155-157	82	17.12	17.10
AP_{11}	$-C_2H_4OCOCH_3$	$-C_2H_4OCOCH_3$	$-NHCOCH_3$	Aniline	517.5	654	100-104	79	12.88	12.84
AP_{12}	$-C_2H_5$	$-C_2H_5$	$-OCH_3$	2-cyno 4-nitro 6-bromo aniline	383.5	661	94-98	85	14.86	14.84

polyester which indicated that wash fastness was good to excellent and the sublimation fastness of all the dyes had the rating 2-4 for polyester which showed sublimation fastness was good. The perspiration and rubbing fastness of all the dyes had the rating 4-5 for polyester which showed perspiration and rubbing fastness was very good to excellent.

Table 2. Shade and fastness properties of dyes on fabrics

Dye No	Shade on polyester	Fastness to		Sublimation on polyester	Perspiration		Rubbing	
		Light	Washing		Acid	Basic	Dry	Wet
AP_1	Tortilla	4	4-5	2	4-5	4	4-5	4
AP_2	Olive	4	4-5	2	4-5	4	4-5	4
AP_3	Ecru	3-4	4-5	2-3	4-5	4-5	4-5	4
AP_4	Pearl Grey	3-4	4-5	3-4	4	4-5	4-5	4
AP_5	Blood Red	4	3-4	2-3	4	4-5	4	4
AP_6	Grey	4-5	4-5	3	4-5	4	4-5	4
AP_7	Peanut	4-5	3-4	3	4-5	4-5	4-5	4
AP_8	Palm Oyster	4-5	4-5	2-3	4	4-5	4-5	4
AP_9	Dijon	4	4-5	2-3	4-5	4-5	4	4
AP_{10}	Egg Nog	4	4-5	3	4-5	4	4	4
AP_{11}	Candy	4-5	3-4	3	4-5	4	4-5	4
AP_{12}	**Biscotti**	**4-5**	**4-5**	**3**	**4**	**4**	**4-5**	**4**

Abbreviations: Light fastness: 1-poor, 2- slight, 3-moderate, 4-fair, 5-good, 6-very good, 7-excellent.
Fastness of washing, sublimation, perspiration, rubbing: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent

CONCLUSION

In summary, a series of new bisazo disperse dyes bearing 3-Amino-4*H*-thieno [3,4-c]chromen- 4 - one have been successfully synthesized by the coupling with different 3° amine coupling component and then with diazotized primary amines fully characterized by elemental analysis, ^1H NMR, UV/VIS and IR. We studied the dyeing of polyester fabrics using bisazo disperse dyes **AP_1-AP_{12}**. These bisazo disperse dyes **(AP_1-AP_{12})** resulting from 3-Amino-4*H*-thieno [3,4-c]chromen-4-one gave tortilla, olive, pearl grey, blood red, peanut, palm, oyster, dijon, egg nog and candy with level dyeing colour shades with fair to excellent washing, light, perspiration, rubbing fastness properties.

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REFERENCES

[1]. H. E. Gaffer, M. Gouda, E. Abdel-Latif, Antibacterial activity of cotton fabrics treated with sulfadimidine azo dye/ chitosan colloid, *Journal of Industrial Textiles*, **2012**, 42(4), 392–399.
[2]. A. A. Fadda, N. S. Abbas, Synthesis of azo disperse dyes containing pyridine ring for dyeing polyester and polyacrylic fibres, *Pigment and Resin Technology*, **2016**, 45(1), 10–17.
[3]. Y. Y. Lams, P. O. Nkeonye, K. A. Bello, M. K. Yakubu, A. O. Lawal, Synthesis of Malononitrile-Condensed Disperse Dyes and Application on Polyester and Nylon Fabrics, *Journal of Textiles*, **2014**, 1-8.
[4]. A. B. Patel, P. I. Vashi, V. D. Patel, D. H. Patel, K. C. Patel and P. S. Patel, Synthesis and Application of Monoazo Reactive Dyes on Silk, Wool and Cotton Fibers, *J. Applicable Chem.*, **2019**, 8(3), 1091-1098.
[5]. N. S. El-Deen, F. F. Hezayen, Ahmed I. M. Koraiem, Novel Heterocyclic Quinone Photosensitizing Dyes, their biological and spectral studies, *J. Applicable Chem.*, **2018**, 7(1), 85-102.
[6]. G. Bagherzade, R. Hosseinabadi, H. Esmaeilpour, Syntheses, Characterization and Spectroscopic Properties of Azo Dyes Using Diethylamine Functionalized Polyethylene Glycol As A Mild, Efficient And Reusable Catalyst, *J. Applicable Chem.*, **2014**, 3(3), 1208-1217.
[7]. N. M. Aljamali, Review in Azo Compounds and its Biological Activity, *Biochem Anal Biochem*, **2015**, 4(2), 1-4.
[8]. S. Harisha, J. Keshavayya, B. E. Kumara Swamy, C. C. Viswanath, Synthesis, characterization and electrochemical studies of azo dyes derived from barbituric acid, *Dyes and Pigments*, **2017**, 136, 742-753.
[9]. Q. Hui-Fen, W. Yin-Ge, D. Yuan, G. Jiao, W. Gang, W. Huang, Structural characterization of a pyrazolone-based heterocyclic dye and its acid-base adduct, *Dyes and Pigments*, **2015**, 112, 67-72.
[10]. E. Gaffer Hatem, M. G. Fouda Moustafa, E. Khalifa Mohamed, Synthesis of Some Novel 2-Amino-5-arylazothiazole Disperse Dyes for Dyeing Polyester Fabrics and Their Antimicrobial Activity, *Molecules*, **2016**, 21,122.
[11]. Rainer Hamprecht, Aloys Westerkamp, Ullmaan's, **2012**, 11, 331-343.
[12]. T. A. Khattab, K. M. Haggag, M. H. Elnagdi, A. A. Abdelrahman, S. A. Aly. Microwave-Assisted Synthesis of Arylazoaminopyrazoles as Disperse Dyes for Textile Printing, *Zeitschrift für anorganische und allgemeine Chemie*, **2016**, 642(13), 766-772.
[13]. B. Karami, K. Eskandari, S. Khodabakhshi. An Efficient Synthesis of New Khellactone-type Compounds using Potassium Hydroxide as Catalyst via One-pot, Three-component Reaction, *Journal of the Iranian Chemical Society*, **2014**, 11, 631–637.
[14]. M. M. Abdou, Utility of 4-hydroxythiocoumarin in Organic Synthesis, *Arabian Journal of Chemistry*, **2017**, 10(2), 3955-3961.
[15]. T. S. Bante, M. M. Rathore. Synthesis and Antimicrobial Activity of Substituted Coumarin and their Derivative, *J. Applicable Chem.*, **2018**, 7(1), 29-32.
[16]. M. Zabradink, *The Production and Application of Fluorescent Brightening Agent*. New York: John Wiley and Sons, **1992**.
[17]. B. B. Raju, T. Varadarajan. Photophysical Properties and Energy Transfer Dye Laser Characteristics of 7-Diethylamino-3-Heteroaryl Coumarin in Solution, *Laser Chemistry*, **1995**, 16, 109-120.

[18]. B. D. Rupnar, P. B. Rokade, P. D. Gaikwad, P. P. Pangrikar, Synthesis of 2-amino-4*H*-Chromenes: A Review, *International Journal of Chemical, Environmental and Biological Sciences*, **2014**, 2(1), 83-84.

[19]. S. Ravichandran, K. Subraman, R. Arunkumar, Synthesis of some Chromene derivatives, *International Journal of Chem Tech Research*, **2009**, 1(2), 329-331.