

# Synthesis of Novel Acid Dyes with Coumarin Moiety and Their Utilization for Dyeing Wool and Silk Fabrics

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## Abstract

This article describes the synthesis of some novel coumarin compounds to use as acid dyes by using compounds 1 - 4 as starting materials, which were prepared by interaction of 2-hydroxybenzaldehyde with ethyl 3-oxobutanoate, diethylmalonate, 4-nitrobenzenediazonium chloride and 4-sulfo benzene-diazonium chloride, respectively. Compound 1 reacted with bromine and 2-cyanoacetohydrazide to give phenacyl bromide derivative 5 and 2-cyanoacetohydrazone derivative 6, respectively. Coupling of compound 6 with equimolar amount of 2-sulfo-4-((4-sulfophenyl) diazenyl)benzenediazonium chloride gave coumarin acid dye 8. Phenacyl bromide derivative 5 reacted with potassium cyanide in refluxing ethanol to produce compound 7, which on coupling with equimolar amount of 8-hydroxy-6-sulfonaphthalene-2-diazonium chloride and 8-hydroxy-3,6-disulfonaphthalene-1-diazonium chloride gave coumarin acid dyes 9 and 10, respectively. Interaction of compound 2 with 2-amino-5-((4-sulfophenyl)diazenyl)benzenesulfonic acid, benzene-1,4-diamine and 3,3'-dimethoxy-[1,1'-biphenyl]-4,4'-diamine in refluxing ethanol afforded compounds 11, 12 and 14, respectively. Diazonium sulphate of compounds 12 and 14 coupling with 4-amino-5-hydroxynaphthalene-2,7-disulfonic acid gave compounds 13 and 15, respectively. Cyclocondensation of compound 3 with ethyl 3-oxobutanoate, diethyl malonate and malononitrile afforded derivatives of 3-acetyl-2H-chromen-2-one 16, ethyl 2-oxo-2H-chromene-3-carboxylate 17 and 2-imino-2H-chromene-3-carbonitrile 18, respectively. Reaction of sodium benzenesulfonate deriva-

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tive **4** with ethyl 3-oxobutanoate and hydrazine hydrate gave compounds **19** and **20**, respectively. The structures of the newly synthesized compounds were confirmed by elemental analysis, UV/VIS, IR,  $^1\text{H}$  NMR and Ms spectral data. The suitability of the prepared dyestuffs for dyeing of wool and silk fabrics has been investigated. The dyed fabric shows good light fastness, very good rubbing, perspiration, washing and excellent sublimation fastness. These dyes have been color shade from blue to violet with very good depth and levelness on fabrics. The dye bath exhaustion and fixation on fabric has been found to be very good.

## Keywords

Synthesis, Coumarin, Acid Dye, Dyeing, Wool Fabric

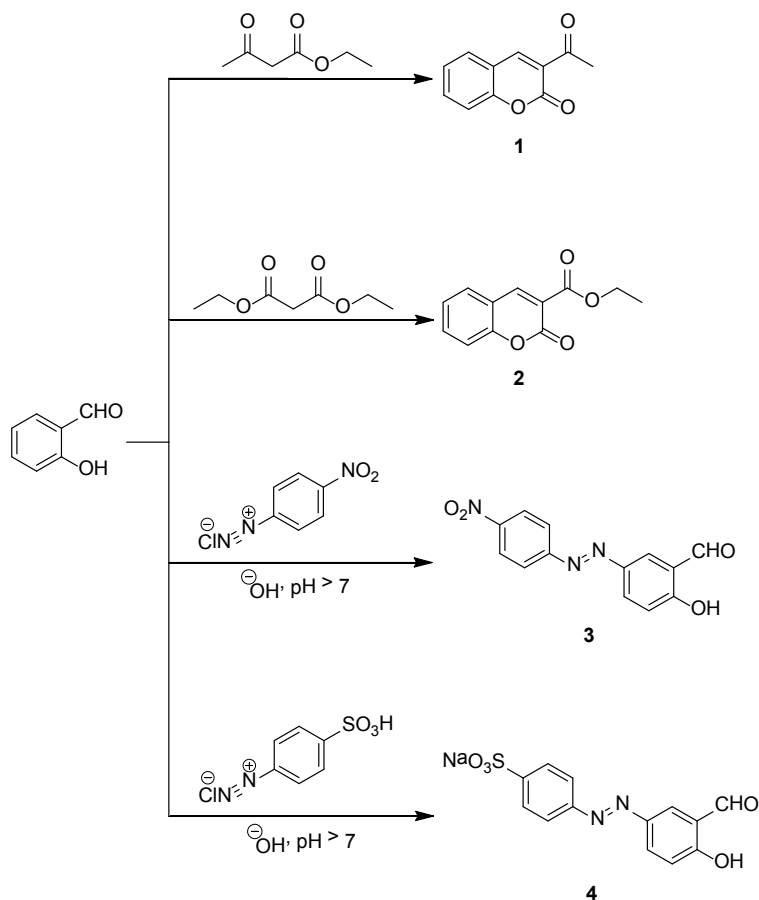
## 1. Introduction

The considerable innovation has been witnessed in past three decades in the field of azo dye chemistry based on heterocyclic systems and studies in the synthesis of such derivatives have been reported [1]-[5]. Most of the recent research has focused on structural variations of existing types, for example, variations in substituent, especially on the side chains of the coupling components. The use of heterocyclic coupling component and diazo components in the synthesis of azo dyes is well established, and the resultant dyes exhibit better tinctorial strength and brighter dyeing than those derived from aniline-based components. Most heterocyclic dyes of technical interest for application to textiles are derived from diazo components consisting of five-membered rings containing one sulphur heteroatom and to which a diazotisable amino group is directly attached. The ring may also possess one or more nitrogen heteroatoms and be fused to another aromatic ring. These diazo components are capable of providing red to blue color dyes that meet the rigorous technical and economical requirements demanded of them by both manufacturer and user. Intensive efforts have been made in the investigation of monoazo dyes in which a heterocyclic system replaces one of the usual carboxylic systems. Many different heterocyclic diazo components have been studied, especially derivatives of thiazole, imidazole, benzimidazole owing to the marked bathochromic effect of such groups [6]-[12]. A majority of acid dyestuffs are sulphonic acid derivatives of azo dyes. The free dye acids are difficult to isolate and are hydroscopic in nature making it difficult to pack and store them. These dyes are invariably isolated as sodium salts. Coumarins are attractive and versatile molecules that find applications in various fields like medicine, perfumery, dyes, pigments, optical brighteners, lasers, optical data storage devices, solar cells [13]-[19]. The coumarin is not fluorescent, but the introduction of an electron-withdrawing group such as a diazotized aromatic amine or an acetyl group makes it highly fluorescent. Coumarin establishes a family of dyes [20]-[24] that are applicable in different fields of science and technology [25]-[27]. The present work was carried out with the following objectives, synthesis and identification of some newly acid dyes based on coumarin derivatives, and the possibility of its use in dyeing of wool and silk fabrics.

## 2. Results and Discussion

### Chemistry

The present investigation deals with the synthesis of novel coumarin compounds to use as acid dyes by using compounds **1-4** as a starting materials, which were prepared by interaction of 2-hydroxybenzaldehyde with ethyl 3-oxobutanoate, diethylmalonate, 4-nitrobenzenediazonium chloride and 4-sulfobenzenediazonium chloride, respectively (**Scheme 1**). Structure of compound **3** was established on the basis of its elemental analysis and spectral data. Thus, IR spectrum of **3** indicated absorption bands at  $\nu_{\text{max}} = 3370\text{ cm}^{-1}$  for hydroxyl group,  $1653\text{ cm}^{-1}$  for carbonyl group and  $1456, 1290\text{ cm}^{-1}$  for nitro group.  $^1\text{H}$  NMR spectrum showed three singlet signals at  $\delta = 8.05, 10.30$  and  $11.78\text{ ppm}$  corresponding to  $\text{H}_6$  of hydroxyphenyl ring, hydroxyl and formyl protons, respectively, two doublet signals, each doublet for two protons at  $\delta = 7.95$  and  $8.32\text{ ppm}$  for  $\text{H}_{2,6}$  and  $\text{H}_{3,5}$  of nitrophenyl ring, respectively, two doublet signals, each doublet for one proton at  $\delta = 7.17$  and  $8.14\text{ ppm}$  due to  $\text{H}_3$  and  $\text{H}_4$  of hydroxyphenyl ring, respectively. IR spectrum of compound **4** showed absorption bands at  $\nu_{\text{max}} = 3462\text{ cm}^{-1}$  for hydroxyl group,  $\nu_{\text{max}} = 1658\text{ cm}^{-1}$  for carbonyl group and  $\nu_{\text{max}} = 1386, 1150\text{ cm}^{-1}$  for sulphate group.  $^1\text{H}$  NMR spectrum showed three singlet signals at  $\delta = 7.19, 10.33$  and  $11.56\text{ ppm}$  corresponding to  $\text{H}_6$  of hydroxyphenyl-

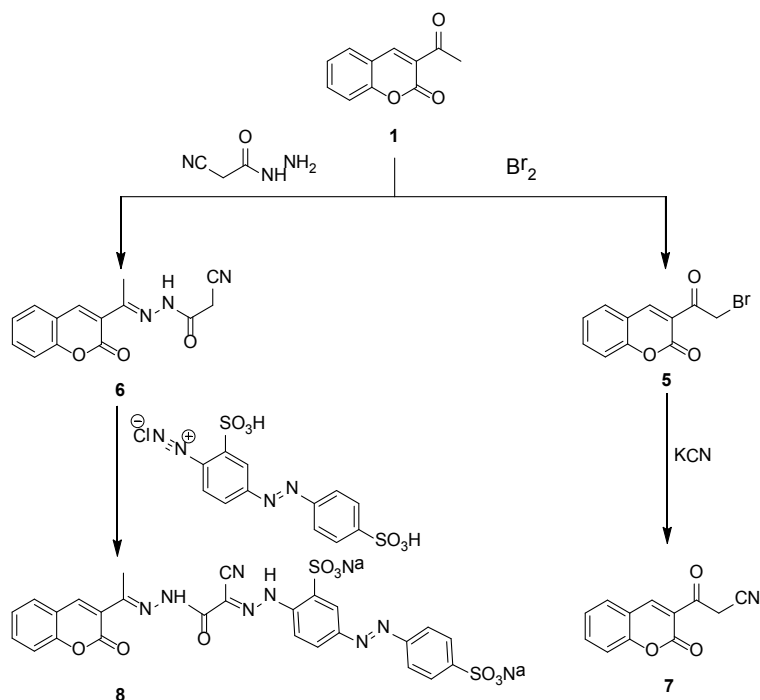


**Scheme 1.** Synthetic pathways for compounds **1-4**.

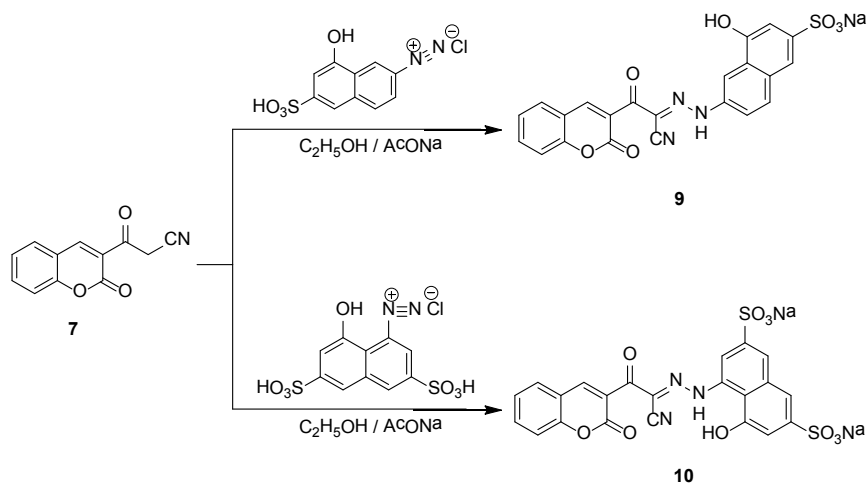
ring, hydroxyl and formyl protons, respectively, two doublet signals, each doublet for two protons at  $\delta = 7.76 - 7.79$  and  $8.15$  ppm for  $H_{2,6}$  and  $H_{3,5}$  of benzenesulfonate ring, respectively, two doublet signals, each doublet for one proton at  $\delta = 7.17$  and  $8.06 - 8.08$  ppm due to  $H_3$  and  $H_4$  of hydroxyphenyl ring, respectively.

3-Acetyl-2*H*-chromen-2-one (**1**) reacted with bromine and 2-cyanoaceto-hydrazide to give phenacyl bromide derivative **5** and 2-cyanoacetohydrazone derivative **6**, respectively. Phenacyl bromide derivative **5** reacted with potassium cyanide in refluxing ethanol to produce 3-oxo propanenitrile derivative **7** (Scheme 2). The structure of compound **7** was established on the basis of their elemental analysis and spectral data. Thus, IR spectrum of compound **7** revealed absorption bands at  $\nu_{\max} = 2207 \text{ cm}^{-1}$  for cyano group,  $\nu_{\max} = 1703$  and  $1636 \text{ cm}^{-1}$  for cyclic carbonyl of coumarin and acyclic carbonyl, respectively. The mass spectrum of compound **7** showed a molecular ion peak at  $m/z = 213$  and a base peak at  $m/z = 101$ . The methylene group in compound **6** proved to be highly reactive. Thus, 2-cyanoacetohydrazone derivative **6** underwent coupling with equimolar amount of 2-sulfo-4-((4-sulfophenyl)-diazonyl)benzenediazonium chloride to give coumarin acid dye **8** (Scheme 2). The IR spectrum of coumarin acid dye **8** showed, two bi-forked characteristic absorption bands at  $\nu_{\max} = 3421$  and  $3350 \text{ cm}^{-1}$  assignable to 2NH groups, another absorption bands at  $\nu_{\max} = 2212 \text{ cm}^{-1}$  for cyano group and at  $\nu_{\max} = 1755$  and  $1657 \text{ cm}^{-1}$  for two carbonyl groups of coumarin ring and amide group, respectively. Mass spectrum of compound **8** showed a molecular ion peak at  $m/z = 681$  and a base peak at  $m/z = 50$ .

3-Oxo-3-(2-oxo-2*H*-chromen-3-yl)propanenitrile (**7**) underwent coupling with equimolar amount of 8-hydroxy-6-sulfonaphthalene-2-diazonium chloride and 8-hydroxy-3,6-disulfonaphthalene-1-diazonium chloride to give coumarin acid dyes **9** and **10**, respectively (Scheme 3). The structure of coumarin acid dyes **9** and **10** were established on the basis of their elemental analysis and spectral data. Thus, IR spectrum of compound **9** revealed absorption bands at  $\nu_{\max} = 3424$  and  $3320 \text{ cm}^{-1}$  for OH and NH groups, respectively,  $\nu_{\max} = 2248 \text{ cm}^{-1}$  for cyano group and at  $\nu_{\max} = 1710$  and  $1632 \text{ cm}^{-1}$  for cyclic carbonyl of coumarin and acyclic carbonyl, respectively.



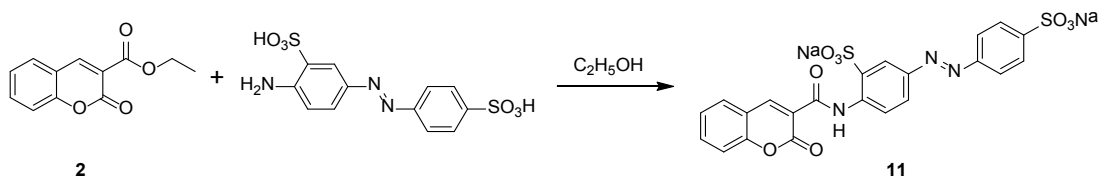
Scheme 2. Synthetic pathways for compounds 5-8.



Scheme 3. Synthetic pathways for compounds 9 and 10.

<sup>1</sup>H NMR spectrum of compound **9** showed two singlet signals at  $\delta = 12.71$  and  $12.80$  ppm corresponding to protons of OH and NH groups. IR spectrum of compound **10** revealed broad absorption band from  $\nu_{\max} = 3486$  to  $3380$  cm<sup>-1</sup> for OH and NH groups,  $\nu_{\max} = 2225$  cm<sup>-1</sup> for cyano group and at  $\nu_{\max} = 1710$  and  $1632$  cm<sup>-1</sup> for cyclic carbonyl of coumarin and acyclic carbonyl, respectively. Mass spectrum of compound **10** showed a molecular ion peak at  $m/z = 587$  and a base peak at  $m/z = 219$ .

Interaction of ethyl 2-oxo-2H-chromene-3-carboxylate (**2**) with 2-amino-5-((4-sulfophenyl)diazenyl) benzene-sulfonic acid in refluxing ethanol afforded coumarin acid dye **11** (Equation 1). The structure of coumarin acid dye **11** was established on the basis of their elemental analysis and spectral data. Thus, IR spectrum of compound **11** revealed absorption bands at  $\nu_{\max} = 3325$  cm<sup>-1</sup> for NH group,  $\nu_{\max} = 1736$  and  $1617$  cm<sup>-1</sup> for two carbonyl groups of coumarin ring and amide group, respectively. Mass spectrum of compound **11** showed a molecular ion peak at  $m/z = 573$  and a base peak at  $m/z = 394$ .



**Equation 1.** Synthetic pathway for compound 11.

Interaction of compound **2** with benzene-1,4-diamine in refluxing ethanol afforded a single product identified as *N*-(4-aminophenyl)-2-oxo-2*H*-chromene-3-carboxamide (**12**) on the basis of elemental analysis and spectral data. Thus, IR spectrum of compound **12** showed, two bi-forked characteristic absorption bands at  $\nu_{\max} = 3458$  and  $3360\text{ cm}^{-1}$  assignable to amino group,  $\nu_{\max} = 3320\text{ cm}^{-1}$  for NH group and  $\nu_{\max} = 1702$  and  $1650\text{ cm}^{-1}$  for two carbonyl groups of coumarin ring and amide group, respectively. Mass spectrum of compound **12** showed a molecular ion peak at  $m/z = 280$  and showed other peaks at  $m/z = 173$  corresponding to fragment ( $M^+ - C_6H_7N_2$ ),  $m/z = 107$  as a base peak for fragment ( $C_6H_7N_2^+$ ) (**Chart 1**).

Compounds **12** was suspended with stirring in concentrated sulfuric acid and cooled to  $0^\circ\text{C} - 5^\circ\text{C}$  then diazotized by adding sodium nitrite. After stirring at  $0^\circ\text{C}$  for 1 h, the diazonium sulphate solution of compound **12** was added to dissolved coupler compound of 4-amino-5-hydroxynaphthalene-2,7-disulfonic acid in 20% sodium hydroxide solution at  $0^\circ\text{C}$  to give compound **13** (**Scheme 4**). IR spectrum of compound **13** revealed broad absorption band from  $\nu_{\max} = 3505$  to  $3273\text{ cm}^{-1}$  for hydroxyl, amino and NH groups and at  $\nu_{\max} = 1700$  and  $1648\text{ cm}^{-1}$  for two carbonyl groups of coumarin ring and amide group, respectively. Mass spectrum of compound **13** showed a molecular ion peak at  $m/z = 654$  and a base peak at  $m/z = 107$ .

In the same manner, compound **2** underwent condensation with 3,3'-dimethoxy-[1,1'-biphenyl]-4,4'-diamine to produce *N*-(4'-amino-3,3'-dimethoxy-[1,1'-biphenyl]-4-yl)-2-oxo-2*H*-chromene-3-carboxamide (**14**). The elemental analysis and spectral data of the latter structure were in agreement with its assigned structure. Thus, IR spectrum of compound **14** revealed a broad absorption band from  $\nu_{\max} = 3400$  to  $3270\text{ cm}^{-1}$  due to amino and NH groups and  $\nu_{\max} = 1718$  and  $1658\text{ cm}^{-1}$  for two carbonyl groups of coumarin ring and amide group, respectively. Besides, the mass spectrum was compatible with the molecular formula  $C_{24}H_{20}N_2O_5$ ,  $m/z = 416$  confirmed structure **14**. Diazonium sulphate of compound **14** coupling with 4-amino-5-hydroxynaphthalene-2,7-disulfonic acid to give compound **15** (**Scheme 5**). IR spectrum of compound **15** revealed a broad absorption band from  $\nu_{\max} = 3509$  to  $3380\text{ cm}^{-1}$  due to hydroxyl, amino and NH groups,  $\nu_{\max} = 1726$  and  $1661\text{ cm}^{-1}$  for two carbonyl groups of coumarin ring and amide group, respectively and  $\nu_{\max} = 1449\text{ cm}^{-1}$  for N=N group. Mass spectrum of compound **15** showed a molecular ion peak at  $m/z = 791$  and a base peak at  $m/z = 64$ .

Cyclocondensation of 2-hydroxy-5-((4-nitrophenyl)diazenyl)benzaldehyde (**3**) with ethyl 3-oxobutanoate, diethyl malonate and/or malononitrile afforded derivatives of 3-acetyl-2*H*-chromen-2-one **16**, ethyl 2-oxo-2*H*-chromene-3-carboxylate **17** and 2-imino-2*H*-chromene-3-carbonitrile **18**, respectively (**Scheme 6**). The structures of compounds **16-18** were established on the basis of their elemental analysis and spectral data. Thus, IR spectrum of compound **16** revealed an absorption bands at  $\nu_{\max} = 1745$  and  $1676\text{ cm}^{-1}$  for two carbonyl groups of coumarin ring and acetyl group, respectively,  $\nu_{\max} = 1522\text{ cm}^{-1}$  corresponding to N=N group and two absorption bands at  $\nu_{\max} = 1338$  and  $1231\text{ cm}^{-1}$  for nitro group.  $^1\text{H}$  NMR spectrum of **16** revealed three singlet signals at  $\delta = 2.53$ ,  $8.42$  and  $8.80\text{ ppm}$  for methyl,  $H_5$  and  $H_4$  of coumarin, respectively, two doublet signals each doublet signal for one proton at  $\delta = 7.65$ ,  $8.25\text{ ppm}$  corresponding to  $H_8$  and  $H_7$  of coumarin, respectively, besides two doublet signals each doublet signal for two protons at  $\delta = 8.08$  and  $8.59\text{ ppm}$  corresponding to  $H_{2,6}$  and  $H_{3,5}$  of nitrophenyl ring, respectively. IR spectrum of compound **17** revealed an absorption bands at  $\nu_{\max} = 1741$  and  $1705\text{ cm}^{-1}$  for two carbonyl groups of coumarin ring and ester group, respectively,  $\nu_{\max} = 1521\text{ cm}^{-1}$  corresponding to N=N group and two absorption bands at  $\nu_{\max} = 1338$  and  $1251\text{ cm}^{-1}$  for nitro group.  $^1\text{H}$  NMR spectrum of **17** revealed triplet and quartet signals at  $\delta = 1.30$  and  $4.30\text{ ppm}$ , respectively corresponding to protons of methyl and methylene of ester group, respectively, two singlet signals at  $\delta = 8.40$  and  $8.89\text{ ppm}$  for  $H_5$  and  $H_4$  of coumarin, respectively, two doublet signals each doublet signal for one proton at  $\delta = 7.60$ ,  $8.19\text{ ppm}$  corresponding to  $H_8$  and  $H_7$  of coumarin, respectively, besides two doublet signals each doublet signal for two protons at  $\delta = 8.03$  and  $8.52\text{ ppm}$  corresponding to  $H_{2,6}$  and  $H_{3,5}$  of nitrophenyl ring, respectively.

IR spectrum of compound **18** revealed an absorption band at  $\nu_{\max} = 3337$  for NH group,  $\nu_{\max} = 2205$  for cyano group,  $\nu_{\max} = 1556\text{ cm}^{-1}$  corresponding to N=N group and two absorption bands at  $\nu_{\max} = 1338$  and  $1251\text{ cm}^{-1}$

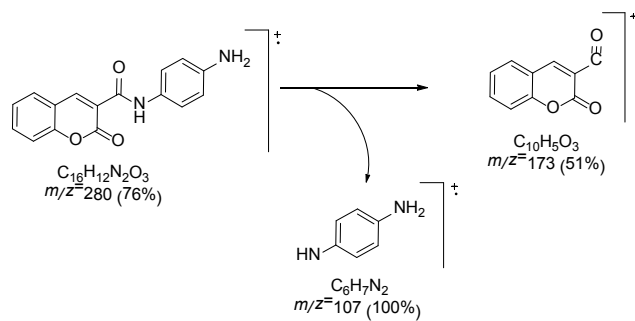
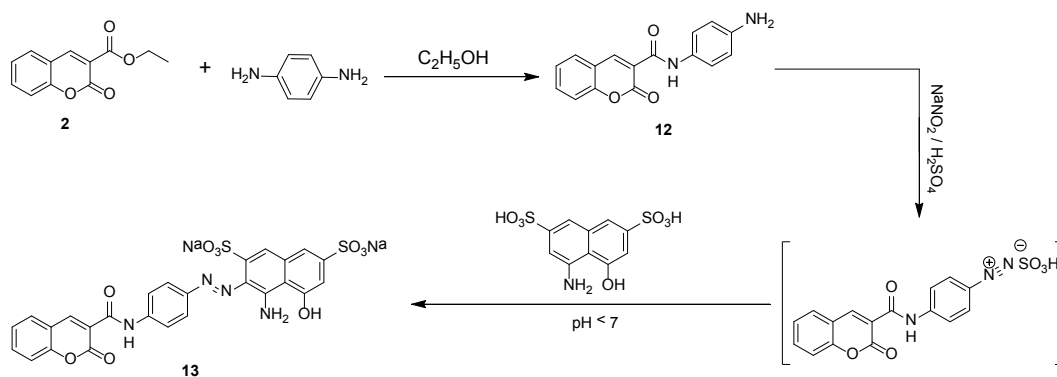
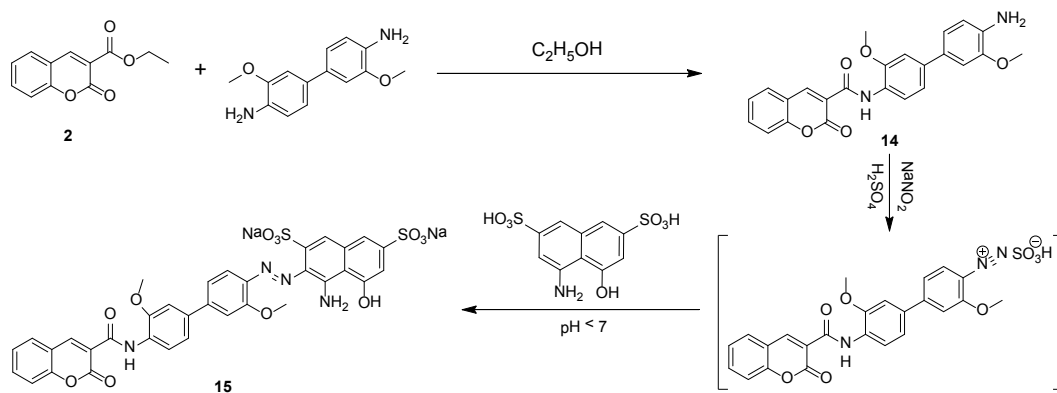


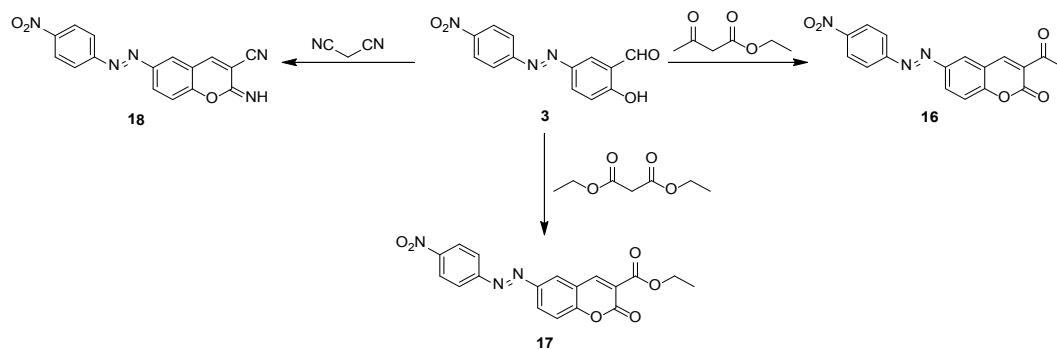
Chart 1. Fragmentation pattern for compound 12.



Scheme 4. Synthetic pathways for compounds 12 and 13.



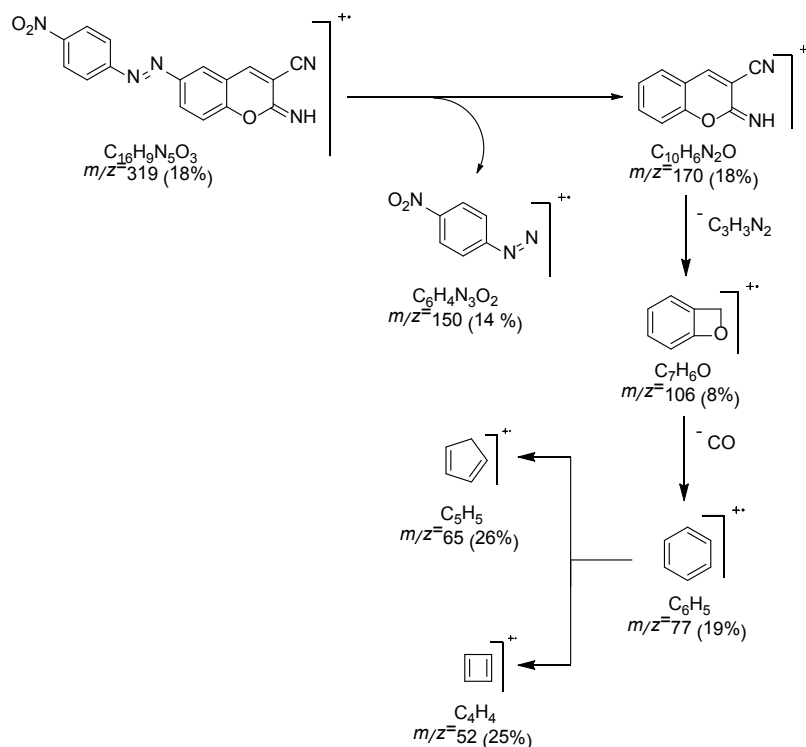
Scheme 5. Synthetic pathways for compounds 14 and 15.



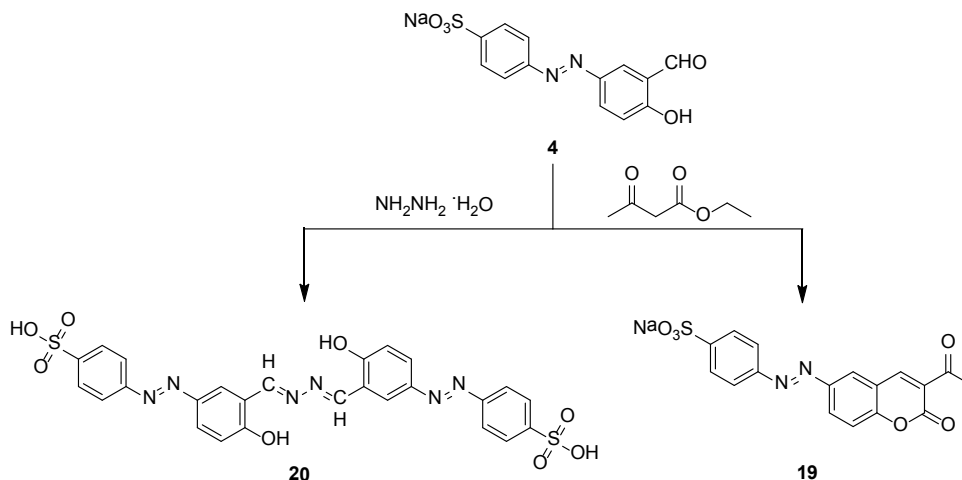
Scheme 6. Synthetic pathways for compounds 16-18.

for nitro group. Mass spectrum of compound **18** showed a molecular ion peak at  $m/z = 321$  ( $M^{+}+2$ ) and showed other peaks at  $m/z = 319$  ( $M^{+}$ ),  $m/z = 170$  corresponding to fragment ( $M^{+}-C_6H_3N_3O_2$ ),  $m/z = 150$  for fragment ( $M^{+}-C_{10}H_5N_2O$ ),  $m/z = 106$  for fragment ( $C_7H_6O^{+}$ ),  $m/z = 77$  for fragment ( $C_6H_5^{+}$ ),  $m/z = 65$  for fragment ( $C_5H_5^{+}$ ) and  $m/z = 52$  for fragment ( $C_4H_4^{+}$ ) (**Chart 2**).

Reaction of sodium benzenesulfonate derivative **4** with ethyl 3-oxobutanoate and/or hydrazine hydrate gave compounds **19** and **20**, respectively (**Scheme 7**). IR spectrum of compound **19** revealed an absorption bands at  $\nu_{\max} = 1754$  and  $1672\text{ cm}^{-1}$  for two carbonyl groups of coumarin ring and acetyl group, respectively,  $\nu_{\max} = 1564\text{ cm}^{-1}$  corresponding to  $N=N$  group and two absorption bands at  $\nu_{\max} = 1382$  and  $1122\text{ cm}^{-1}$  for  $SO_2$  group.  $^1H$  NMR spectrum of **19** revealed triplet signal at  $\delta = 2.57$  ppm corresponding to protons of methyl group, two singlet signals at  $\delta = 8.19$  and  $8.80$  ppm for  $H_5$  and  $H_4$  of coumarin, respectively, two doublet signals each



**Chart 2.** Fragmentation pattern for compound **18**.



**Scheme 7.** Synthetic pathways for compounds **19** and **20**.

doublet signal for one proton at  $\delta = 7.62$ , 7.85 ppm corresponding to H<sub>8</sub> and H<sub>7</sub> of coumarin, respectively, besides two doublet signals each doublet signal for two protons at  $\delta = 7.78$  and 8.52 ppm corresponding to H<sub>2,6</sub> and H<sub>3,5</sub> of benzenesulfonate ring, respectively.

IR spectrum of compound **20** revealed an absorption broad band at  $\nu_{\max} = 3384$  for OH groups,  $\nu_{\max} = 1486$  cm<sup>-1</sup> corresponding to N=N group and two absorption bands at  $\nu_{\max} = 1384$  and 1132 cm<sup>-1</sup> for SO<sub>2</sub> group. Mass spectrum of compound **20** showed a molecular ion peak at  $m/z = 552$  (M<sup>+</sup>-2N<sub>2</sub>) and showed other peaks at  $m/z = 450$  corresponding to fragment (C<sub>20</sub>H<sub>15</sub>N<sub>6</sub>O<sub>5</sub>S<sup>+</sup>) and  $m/z = 295$  for fragment (C<sub>14</sub>H<sub>10</sub>N<sub>6</sub>O<sub>2</sub><sup>+</sup>) (**Chart 3**).

### 3. Experimental

#### 3.1. Methods and Materials

##### 3.1.1. Wool Fabric

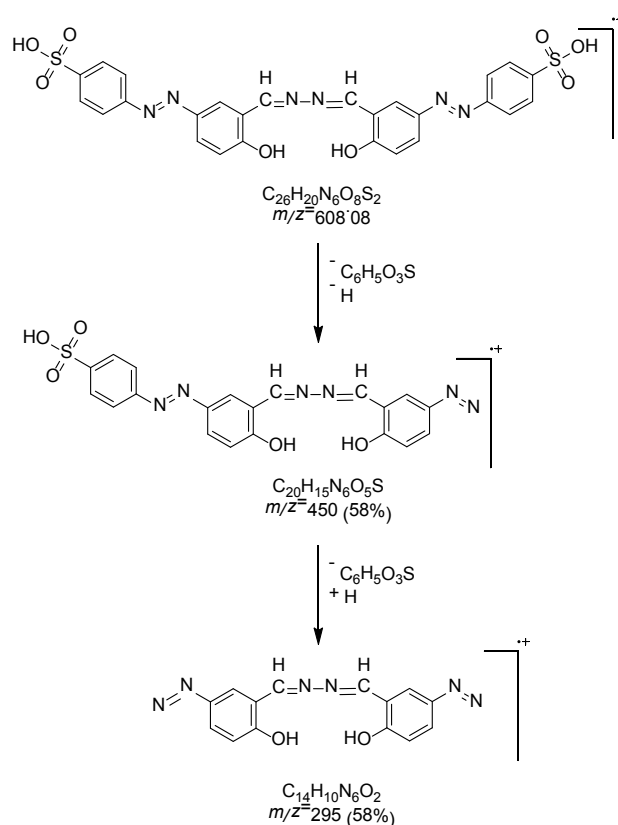
Wool fabric of 310 g/m<sup>2</sup>, supplied by Golden Tex Co., Tenth of Ramadan-Egypt, was initially treated in an aqueous solution with a liquor ratio 50:1 containing 0.5 g/L sodium carbonate and 2 g/L nonionic detergent at 60°C for 30 min, then thoroughly washed, and air dried at room temperature.

##### 3.1.2. Silk Fabric

Degummed and bleached silk fabric (El-Khateib Co., Egypt) weighing 90 g/m<sup>2</sup> was used throughout this work. Before dyeing, the fabric was treated in an aqueous solution containing 2 g/l non-ionic detergent for 1 h at 90°C and at a liquor ratio 50:1, then washed thoroughly in water and air dried at room temperature.

##### 3.1.3. Chemicals

H-acid,  $\gamma$ -acid and 4-aminoazobenzene-3,4'-disulphonic acid, 1-amino-3-bromo-5,10-dioxoanthracene-2-sulphonic acid were obtained from Fluka Chemie AG. All other chemicals used in the study were of reagent grade and applied without further purification.



**Chart 3.** Fragmentation pattern for compound **20**.



### 3.2. Chemistry

Melting points (°C, uncorrected) were determined in open capillaries on a Gallen Kemp melting point apparatus (Sanyo Gallen Kemp, Southborough, UK). IR spectra (KBr) were recorded on FT-IR 5300 spectrometer and Perkin Elmer spectrum RXIFT-IR system ( $\nu$ ,  $\text{cm}^{-1}$ ). Pre-coated silica gel plates (silica gel 0.25 mm, 60 G F 254; Merck, Germany) were used for thin layer chromatography. The NMR spectra in ( $\text{DMSO}-d_6$ ) were recorded at 400 MHz on a Varian Gemini NMR spectrometer ( $\delta$ , ppm). Mass spectra were obtained on GC Ms-QP 1000 EX mass spectrometer at 70 eV. Elemental analyses were performed on Carlo Erba 1108 Elemental Analyzer (Heraeus, Hanau, Germany). All compounds were within  $\pm 0.4\%$  of the theoretical values. Analyses were carried out by the Micro analytical Research Center, Faculty of Science, Cairo University and Al-Azhar University.

#### 3.2.1. 3-Acetyl-2H-Chromen-2-One (1)

Compound **1** was synthesized according to the literature procedure [28].

#### 3.2.2. Ethyl 2-Oxo-2H-Chromene-3-Carboxylate (2)

Compound **2** was synthesized according to the literature procedure [29].

#### 3.2.3. 2-Hydroxy-5-((4-Nitrophenyl)Diazenyl)Benzaldehyde (3)

2-Hydroxybenzaldehyde (1.22 g, 0.01 mol) was dissolved in water (20 mL) containing (0.4 g, 0.01 mol) of sodium hydroxide and (4.24 g, 0.04 mol) of sodium carbonate during the period of 30 min at 0°C. The resulting solution was added slowly to a solution of diazonium chloride of 4-nitroaniline (1.38 g, 0.01 mol) in water at 0°C - 5°C. The reaction mixture was stirred for 1 h at 0°C and then allowed to warm slowly to room temperature. The product was collected by filtration and washed with 100 mL of NaCl solution (10%) under vacuum. The obtained solid was dried under vacuum at 80°C overnight to give **3**. Brown crystals, yield, 92%; mp 185-188°C. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3370 (OH), 1653 (C=O), 1578 (C=C), 1526 (N=N), 1456, 1290  $\text{cm}^{-1}$  ( $\text{NO}_2$ ).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  = 7.17 (1H, d, Ar- $\text{H}_3$ ), 7.95 (2H, d, nitrophenyl- $\text{H}_{2,6}$ ), 8.05 (1H, s, Ar- $\text{H}_6$ ), 8.14 (1H, d, Ar- $\text{H}_4$ ), 8.32 (2H, d, nitrophenyl- $\text{H}_{3,5}$ ), 10.30 ppm (1H, s, OH), 11.78 (1H, s, CHO). Anal. Calcd. for  $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_4$  (271.23): C, 57.57; H, 3.34; N, 15.49. Found: C, 57.29; H, 3.56; N, 15.28%.

#### 3.2.4. Sodium 4-((3-Formyl-4-Hydroxyphenyl)Diazenyl)Benzenesulfonate (4)

2-Hydroxybenzaldehyde (1.22 g, 0.01 mol) was dissolved in water (20 mL) containing (0.40 g, 0.01 mol) of sodium hydroxide and (4.24 g, 0.04 mol) of sodium carbonate during the period of 30 min at 0°C. The resulting solution was added slowly to a solution of 4-sulfobenzenediazonium chloride (2.2 g, 0.01 mol) in water at 0°C - 5°C. The reaction mixture was stirred for 1 h at 0°C and then allowed to warm slowly to room temperature. The product was collected by filtration and washed with 100 mL of NaCl solution (10%) under vacuum. The obtained solid was dried under vacuum at 80°C overnight to give **4**. Yellow crystals, yield: 61%; mp 350°C - 351°C (dec.). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3462 (OH), 1658 (C=O), 1558 (C=C), 1478 (N=N), 1386, 1150  $\text{cm}^{-1}$  ( $\text{SO}_2$ ).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  = 7.17 (1H, d, Ar- $\text{H}_3$ ), 7.19 (1H, s, Ar- $\text{H}_6$ ), 7.76 - 7.79 (2H, d, benzenesulfonate- $\text{H}_{2,6}$ ), 8.06-8.08 (1H, d, Ar- $\text{H}_4$ ), 8.15 (2H, d, benzenesulfonate- $\text{H}_{3,5}$ ), 10.33 (1H, s, OH), 11.56 ppm (1H, s, CHO). Anal. Calcd. for  $\text{C}_{13}\text{H}_9\text{N}_2\text{NaO}_5\text{S}$  (328.28): C, 47.56; H, 2.76; N, 8.53; S, 9.77. Found: C, 47.21; H, 3.03; N, 8.18; S, 10.02%.

#### 3.2.5. 3-(2-Bromoacetyl)-2H-Chromen-2-One (5)

Compound **1** was synthesized according to the literature procedure [30].

#### 3.2.6. 2-Cyano-*N'*-(1-(2-Oxo-2H-Chromen-3-yl)Ethylidene)Acetohydrazide (6)

Compound **1** was synthesized according to the literature procedure [31].

#### 3.2.7. 3-Oxo-3-(2-Oxo-2H-Chromen-3-yl)Propanenitrile (7)

A mixture of 3-(2-bromoacetyl)-2H-chromen-2-one (**5**; 2.66 g, 0.01 mol) and potassium cyanide (0.65 g, 0.01 mol) in ethanol (20 mL) was heated under reflux for 4 h. during the reflux period, a brown crystalline solid was separated. The separated solid was filtered off, washed with ethanol and recrystallized from ethanol to give **7**. Brown crystals, yield 62%; mp 180°C - 182°C. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 2931 (CH-aliphatic), 2207 ( $\text{C}\equiv\text{N}$ ), 1703

(O=C=O), 1636 (C=O). MS  $m/z$  (%): 213 [ $M^+$ ] (99), 175 (27), 134 (47), 101 (100). Anal. Calcd. for  $C_{12}H_7NO_3$  (213.19): C, 67.61; H, 3.31; N, 6.57. Found: C, 67.09; H, 3.13; N, 7.02%.

### 3.2.8. Sodium 2-(2-(1-Cyano-2-Oxo-2-(2-(1-(2-oxo-2*H*-Chromen-3-yl)Ethylidene)Hydr-Aziny)Ethylidene)Hydraziny)-5-((4-Sulfonatophenyl)Diazenyl)Benzenesulfonate (8)

To a stirred solution of (6; 2.69 g, 0.01 mol) in ethanol (50 mL) containing, sodium acetate (3 g), 2-sulfo-4-((4-sulfophenyl)diazenyl)benzenediazonium chloride (prepared by adding sodium nitrite (0.69 g, 0.01 mol) to 2-amino-5-((4-sulfophenyl)diazenyl)benzenesulfonic acid (3.57 g, 0.01 mol) in conc. HCl (6 mL) at (0°C - 5°C) under stirring) was added drop wise while cooling to (0°C - 5°C) and stirring. The reaction mixture was then left at room temperature for 2 h and the solid product formed was collected by filtration and recrystallized from DMF/acetone to give 8. Orange crystals, yield, 82%; mp >300°C.  $\lambda_{max}$  (H<sub>2</sub>O) 518 nm. IR (KBr,  $cm^{-1}$ ):  $\nu_{max}$  = 3421, 3350 (2NH), 2929 (CH-aliphatic), 2212 (C≡N), 1755 (O-C=O), 1657  $cm^{-1}$  (C=O). MS  $m/z$  (%): 681 [ $M^+$ ] (5), 356 (77), 310 (32), 267 (78), 50 (100). Anal. Calcd. for  $C_{26}H_{17}N_7Na_2O_9S_2$  (681.56): C, 45.82; H, 2.51; N, 14.39; S, 9.41. Found: C, 45.25; H, 2.69; N, 15.35; Na, 6.09; S, 8.98, O, 21.60%.

### 3.2.9. General Procedure for Preparation of Compounds 9 and 10

To a stirred solution of (7; 2.13 g, 0.01 mol) in ethanol (50 mL) containing, sodium acetate (3 g) 8-hydroxy-6-sulfonaphthalene-2-diazonium chloride and/or 8-hydroxy-3,6-disulfonaphthalene-1-diazonium chloride (prepared by adding sodium nitrite (0.69 g, 0.01 mol) to 6-amino-4-hydroxynaphthalene-2-sulfonic acid and/or 4-amino-5-hydroxynaphthalene-2,7-disulfonic acid (0.01 mol) in conc. HCl (6 mL) at (0°C - 5°C) under stirring) was added drop wise while cooling to (0°C - 5°C) and stirring. The reaction mixture was then left at room temperature for 2 h and the solid product formed was collected by filtration and recrystallized from the appropriate solvents to afford colored products 9 and 10, respectively.

#### 1) Sodium 6-(2-(1-cyano-2-oxo-2-(2-oxo-2*H*-chromen-3-yl)ethylidene)hydraziny)-4-hydroxynaphthalene-2-sulfonate (9)

Violet crystals, yield, 88%; mp >300°C (DMF/acetone),  $\lambda_{max}$  (H<sub>2</sub>O) 545 nm. IR (KBr,  $cm^{-1}$ ):  $\nu_{max}$  = 3424 (OH), 3320 (NH), 2907 (CH-aliphatic), 2248 (C≡N), 1710 (O-C=O), 1632  $cm^{-1}$  (C=O). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 7.22 - 8.81 (10H, m, 2Ar-H + coumarin-H<sub>4,8</sub>), 12.71, 12.80 ppm (2H, 2s, OH, NH). Anal. Calcd. for  $C_{22}H_{12}N_3NaO_7S$  (485.40): C, 54.44; H, 2.49; N, 8.66; S, 6.61. Found: C, 54.84; H, 2.56; N, 8.32; S, 6.07%.

#### 2) Sodium 4-(2-(1-cyano-2-oxo-2-(2-oxo-2*H*-chromen-3-yl)ethylidene)hydraziny)-5-hydroxynaphthalene-2,7-disulfonate (10)

Violet crystals, yield, 88%; mp >300°C (DMF/acetone),  $\lambda_{max}$  (H<sub>2</sub>O) 520 nm. IR (KBr,  $cm^{-1}$ ):  $\nu_{max}$  = 3486 - 3380 (OH, NH), 2225 (C≡N), 1710 (O-C=O), 1632  $cm^{-1}$  (C=O). MS  $m/z$  (%): 587 [ $M^+$ ] (23), 537 (52), 506 (18), 358 (71), 219 (100). Anal. Calcd. for  $C_{22}H_{11}N_3Na_2O_{10}S_2$  (587.45): C, 44.98; H, 1.89; N, 7.15; S, 10.92. Found: C, 45.04; H, 2.02; N, 6.96; S, 11.06%.

### 3.2.10. General Procedure for Preparation of Compounds 11, 12, 14

Interaction of ethyl 2-oxo-2*H*-chromene-3-carboxylate (2; 2.18 g, 0.01 mol) with aromatic aryl amine derivatives namely, 2-amino-5-((4-sulfophenyl)diazenyl)-benzenesulfonic acid, benzene-1,4-diamine and/or 3,3'-dimethoxy-[1,1'-biphenyl]-4,4'-diamine (0.01 mol) in ethanol (20 mL) was heated under reflux for 4 h. The separated solid was filtered off, washed with ethanol and recrystallized from the appropriate solvents to give the compounds 11, 12 and 14, respectively.

#### 1) Sodium 2-(2-oxo-2*H*-chromene-3-carboxamido)-5-((4-sulfonatophenyl)-diazenyl)benzenesulfonate (11)

Yellow crystals, yield, 91%; mp >300°C (DMF/acetone),  $\lambda_{max}$  (H<sub>2</sub>O) 440 nm. IR (KBr,  $cm^{-1}$ ):  $\nu_{max}$  = 3325 (NH), 3060 (CH-aromatic), 1736 (O-C=O), 1617 (C=O), 1509  $cm^{-1}$  (N=N). MS  $m/z$  (%): 573 [ $M^+$ ] (2), 448 (99), 394 (100), 358 (78), 246 (86). Anal. Calcd. for  $C_{22}H_{13}N_3Na_2O_9S_2$  (573.46): C, 46.08; H, 2.28; N, 7.33; S, 11.18. Found: C, 45.89; H, 2.12; N, 7.96; S, 11.36%.

#### 2) *N*-(4-aminophenyl)-2-oxo-2*H*-chromene-3-carboxamide (12)

Bright orange crystals, yield, 65%; mp 233°C - 235°C (AcOH). IR (KBr,  $cm^{-1}$ ):  $\nu_{max}$  = 3458, 3360 (NH<sub>2</sub>), 3320 (NH), 3020 (CH-aromatic), 1702 (O-C=O), 1650  $cm^{-1}$  (C=O). MS  $m/z$  (%): 280 [ $M^+$ ] (76), 173 [ $M^+$ -C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>] (51), 107 [C<sub>6</sub>H<sub>7</sub>N<sub>2</sub><sup>+</sup>] (100) (**Chart 1**). Anal. Calcd. for  $C_{16}H_{12}N_2O_3$  (280.28): C, 68.56; H, 4.32; N, 9.99. Found: C, 68.25; H, 4.51; N, 10.06%.

#### 3) *N*-(4'-amino-3,3'-dimethoxy-[1,1'-biphenyl]-4-yl)-2-oxo-2*H*-chromene-3-carboxamide (14)

Brownish-yellow crystals, yield, 70%; mp 110°C - 112°C (DMF/acetone). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3400-3270 ( $\text{NH}_2$ , NH), 3183 (CH-aromatic), 2935 (CH-aliphatic), 1718 (O-C=O), 1658  $\text{cm}^{-1}$  (C=O). MS  $m/z$  (%): 416 [ $\text{M}^+$ ] (1), 244 (74), 201 (100), 186 (35), 158 (36). Anal. Calcd. for  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_5$  (416.43): C, 69.22; H, 4.84; N, 6.73. Found: C, 68.97; H, 5.01; N, 6.86%.

### 3.2.11. Sodium 4-Amino-5-Hydroxy-3-((4-(2-Oxo-2*h*-Chromene-3-Carboxamido)Phenyl)-Diazenyl)Naphthalene-2,7-Disulfonate (13)

Compounds **12** (2.80 g, 0.01 mol) was suspended with stirring in concentrated  $\text{H}_2\text{SO}_4$  (3 mL) and cooled to 0°C - 5°C then diazotized by adding  $\text{NaNO}_2$  (0.9 g, 0.013 mol) drop wise at 0°C - 5°C. After stirring at 0°C for 1h, the diazonium sulphate solution of compound **12** were checked with starch paper for the presence of  $\text{HNO}_2$ . There were a colour change from white to brown, sulfamic acid was added to destroy excess  $\text{HNO}_2$ . Coupler compound 4-amino-5-hydroxynaphthalene-2,7-disulfonic acid (3.19 g, 0.01 mol) was dissolved in NaOH solution (3 mL, 20%) at 0°C. The cold solution of diazo compound **12** that were prepared above were added to this solution, keeping the temperature at 0°C - 5°C and maintaining pH 4 by adding AcONa. After stirring for 1 h at 0°C, the dyest **13** was collected by filtration then recrystallized from DMF/acetone. Violet crystals, yield, 89%; mp >300°C,  $\lambda_{\text{max}}(\text{H}_2\text{O})$  570 nm. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3505 - 3273 (OH,  $\text{NH}_2$ , NH), 3073 (CH-aromatic), 1700 (O-C=O), 1648 (C=O), 1502  $\text{cm}^{-1}$  (N=N). MS  $m/z$  (%): 654 [ $\text{M}^+$ ] (4), 486 (5), 280 (71), 173 (50), 107 (100). Anal. Calcd. for  $\text{C}_{26}\text{H}_{16}\text{N}_4\text{Na}_2\text{O}_{10}\text{S}_2$  (654.54): C, 47.71; H, 2.46; N, 8.56; S, 9.80. Found: C, 47.29; H, 3.01; N, 8.86; S, 10.16%.

### 3.2.12. Sodium 4-Amino-3-((3,3'-Dimethoxy-4'-(2-Oxo-2*h*-Chromene-3-Carboxamido)-[1,1'-Bi-Phenyl]-4-yl)Diazenyl)-5-Hydroxynaphthalene-2,7-Disulfonate (15)

Compounds **14** (4.16 g, 0.01 mol) was suspended with stirring in concentrated  $\text{H}_2\text{SO}_4$  (3 mL) and cooled to 0°C - 5°C then diazotized by adding  $\text{NaNO}_2$  (0.9 g, 0.013 mol) drop wise at 0°C - 5°C. After stirring at 0°C for 1h, the diazonium sulphate solution of compound **14** were checked with starch paper for the presence of  $\text{HNO}_2$ . There were a colour change from white to brown, sulfamic acid was added to destroy excess  $\text{HNO}_2$ . Coupler compound 4-amino-5-hydroxynaphthalene-2,7-disulfonic acid (3.19 g, 0.01 mol) was dissolved in NaOH solution (3 mL, 20%) at 0°C. The cold solution of diazo compound **14** that were prepared above were added to this solution, keeping the temperature at 0-5°C and maintaining pH 4 by adding AcONa. After stirring for 1h at 0°C, the dyest **15** was collected by filtration then recrystallized from DMF/acetone. Violet crystals, yield, 89%; mp >300°C,  $\lambda_{\text{max}}(\text{H}_2\text{O})$  405 nm. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3509 - 3380 (OH,  $\text{NH}_2$ , NH), 1726 (O-C=O), 1661 (C=O), 1449  $\text{cm}^{-1}$  (N=N). MS  $m/z$  (%): 791 [ $\text{M}^+ + 1$ ] (5), 744 (8), 472 (9), 146 (52), 118 (63), 64 (100). Anal. Calcd. for  $\text{C}_{34}\text{H}_{24}\text{N}_4\text{Na}_2\text{O}_{12}\text{S}_2$  (790.68): C, 51.65; H, 3.06; N, 7.09; S, 8.11. Found: C, 51.29; H, 2.96; N, 6.86; S, 7.92%.

### 3.2.13. General Procedure for Preparation of Compounds 16 - 18

To a mixture of 2-hydroxy-5-((4-nitrophenyl)diazenyl)benzaldehyde (**3**, 2.71 g, 0.01 mol) and ethyl 3-oxobutanoate, diethyl malonate and/or malononitrile (0.01 mol) in ethanol (20 mL), glacial AcOH (0.3 mL) and piperidine (0.3 mL) were added under rapid stirring. The reaction mixture was heated under reflux for 5 h and left to cool, the solid formed after cooling filtered off and recrystallized from a suitable solvent to afford the pure products **16-18**, respectively.

#### 1) 3-Acetyl-6-((4-nitrophenyl)diazenyl)-2*h*-chromen-2-one (16)

Brown crystals, yield, 59%; mp 225-227°C (DMF). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3050 (CH-aromatic), 2928 (CH-aliphatic), 1745 (O-C=O), 1676 (C=O), 1600 (C=C), 1522 (N=N), 1338, 1231  $\text{cm}^{-1}$  ( $\text{NO}_2$ ).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  = 2.53 (3H, s,  $\text{CH}_3$ ), 7.65 (1H, d, coumarin- $\text{H}_8$ ), 8.08 (2H, d, nitrophenyl- $\text{H}_{2,6}$ ), 8.25 (1H, d, coumarin- $\text{H}_7$ ), 8.42 (1H, s, coumarin- $\text{H}_5$ ), 8.59 (2H, d, nitrophenyl- $\text{H}_{3,5}$ ), 8.80 ppm (1H, s, coumarin- $\text{H}_4$ ). Anal. Calcd. for  $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_5$  (337.29): C, 60.54; H, 3.29; N, 12.46. Found: C, 60.30; H, 3.48; N, 12.28%.

#### 2) ethyl 6-((4-nitrophenyl)diazenyl)-2-oxo-2*h*-chromene-3-carboxylate (17)

Brown crystals, yield, 56%; mp 245°C - 246°C (DMF). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3097 (CH-aromatic), 2960 (CH-aliphatic), 1741 (coumarin C=O), 1705 (ester C=O), 1521 (N=N), 1338, 1251  $\text{cm}^{-1}$  ( $\text{NO}_2$ ).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  = 1.30 (3H, t,  $\text{CH}_3$ ), 4.30 (2H, q,  $\text{CH}_2$ ), 7.60 (1H, d, coumarin- $\text{H}_8$ ), 8.03 (2H, d, nitrophenyl- $\text{H}_{2,6}$ ), 8.19 (1H, d, coumarin- $\text{H}_7$ ), 8.40 (1H, s, coumarin- $\text{H}_5$ ), 8.52 (2H, d, nitrophenyl- $\text{H}_{3,5}$ ), 8.89 ppm (1H, s, coumarin- $\text{H}_4$ ). Anal. Calcd. for  $\text{C}_{18}\text{H}_{13}\text{N}_3\text{O}_6$  (367.31): C, 58.86; H, 3.57; N, 11.44. Found: C, 60.01; H, 3.34; N, 11.68%.

### 3) 2-imino-6-((4-nitrophenyl)diazenyl)-2*h*-chromene-3-carbonitrile (18)

Brown crystals, yield, 56%; mp 250-252°C (dec.) (DMF). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3337 (NH), 2205 ( $\text{C}\equiv\text{N}$ ), 1605 ( $\text{C}=\text{N}$ ), 1556 ( $\text{N}=\text{N}$ ), 1336, 1246  $\text{cm}^{-1}$  ( $\text{NO}_2$ ). MS  $m/z$  (%): 321 [ $\text{M}^++2$ ] (11), 319 [ $\text{M}^+$ ] (18), 300 (100), 170 [ $\text{M}^+-\text{C}_6\text{H}_3\text{N}_3\text{O}_2$ ] (18), 150 [ $\text{M}^+-\text{C}_{10}\text{H}_5\text{N}_2\text{O}$ ] (14), 106 [ $\text{C}_7\text{H}_6\text{O}^+$ ] (8), 77 [ $\text{C}_6\text{H}_5^+$ ] (19), 65 [ $\text{C}_5\text{H}_5^+$ ] (26), 52 [ $\text{C}_4\text{H}_4^+$ ] (25) (**Chart 2**). Anal. Calcd. for  $\text{C}_{16}\text{H}_9\text{N}_5\text{O}_3$  (319.27): C, 60.19; H, 2.84; N, 21.94. Found: C, 59.94; H, 3.01; N, 22.05%.

#### 3.2.14. Sodium 4-((3-Acetyl-2-Oxo-2*h*-Chromen-6-yl)Diazenyl)Benzenesulfonate (19)

To a mixture of sodium 4-((3-formyl-4-hydroxyphenyl)diazenyl)benzene-sulfonate (**4**, 3.28 g, 0.01 mol) and ethyl 3-oxobutanoate (1.30 g, 0.01 mol) in ethanol (20 mL), glacial AcOH (0.3 mL) and piperidine (0.3 mL) were added under rapid stirring. The reaction mixture was heated under reflux for 5 h and, after cooling, the solid was filtered and recrystallized from DMF/acetone to afford the pure product **19**. Bright yellow crystals, yield, 63%; mp > 360°C (dec.). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3058 (CH-aromatic), 2922 (CH-aliphatic), 1754 (O-C=O), 1672 (C=O), 1620 (C=C), 1564 ( $\text{N}=\text{N}$ ), 1382, 1122  $\text{cm}^{-1}$  ( $\text{SO}_2$ ).  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  = 2.57 (3H, t,  $\text{CH}_3$ ), 7.62 (1H, d, coumarin- $\text{H}_8$ ), 7.78 (2H, d, Ar- $\text{H}_{2,6}$ ), 7.85 (1H, d, coumarin- $\text{H}_7$ ), 8.19 (1H, s, coumarin- $\text{H}_5$ ), 8.52 (2H, d, Ar- $\text{H}_{3,5}$ ), 8.80 ppm (1H, s, coumarin- $\text{H}_4$ ). Anal. Calcd. for  $\text{C}_{17}\text{H}_{11}\text{N}_2\text{NaO}_6\text{S}$  (394.33): C, 51.78; H, 2.81; N, 7.10; S, 8.13. Found: C, 52.01; H, 3.05; N, 6.94; S, 7.95%.

#### 3.2.15. 4,4'-(((Hydrazine-1,2-Diylidenebis(Methanylylidene)))Bis(4-Hydroxy-3,1-Phenyl-Ene)) Bis(Diazeno-2,1-diyl))Dibenzenesulfonic Acid (20)

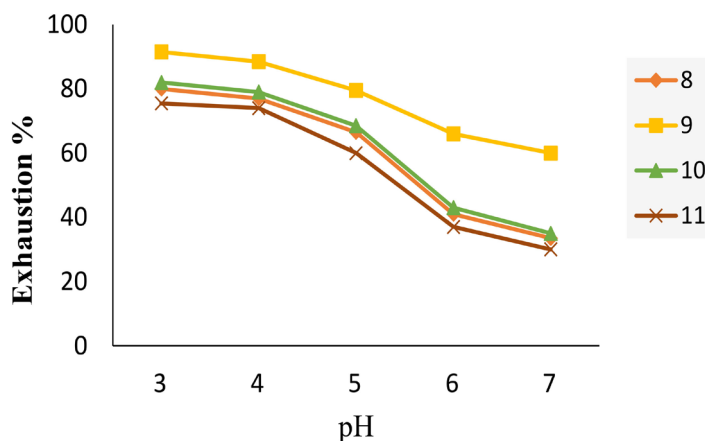
A mixture of sodium 4-((3-formyl-4-hydroxyphenyl)diazenyl)benzenesulfonate (**4**, 6.56 g, 0.02 mol) and hydrazine hydrate (0.5 g, 0.01 mol) in ethanol (30 mL) were refluxed for 2 h. The reaction mixture was concentrated and left to cool then recrystallized from DMF/acetone to give **20**. Bright yellow crystals, yield, 63%; mp 320°C - 322°C (dec.). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3384 (OH), 3108 (CH-aromatic), 2934 (CH-aliphatic), 1600 ( $\text{C}=\text{N}$ ), 1486 ( $\text{N}=\text{N}$ ), 1384, 1132  $\text{cm}^{-1}$  ( $\text{SO}_2$ ). MS  $m/z$  (%): 552 [ $\text{M}^+-2\text{N}_2$ ] (60), 450 [ $\text{C}_{20}\text{H}_{15}\text{N}_6\text{O}_5\text{S}^+$ ] (58), 295 [ $\text{C}_{14}\text{H}_{10}\text{N}_6\text{O}_2^+$ ] (58), 80 (100) (**Chart 3**). Anal. Calcd. for  $\text{C}_{26}\text{H}_{20}\text{N}_6\text{O}_8\text{S}_2$  (608.60): C, 51.31; H, 3.31; N, 13.81; S, 10.54. Found: C, 51.61; H, 2.95; N, 14.02; S, 10.15%.

## 4. Dyeing of Coumarin Compounds 8-11

### 4.1. Dyeing of Coumarin Compounds 8-11 on Wool

#### 4.1.1. Effect of pH and Dyeing Temperature on Percent of Dyeing Exhaustion

**Table 1** and **Figure 1** show the effect of pH on the exhaustion of acid dyes on wool fibre. The data revealed that at lower dyeing pH values (pH 4), the substantivity of the acid dyes on wool was virtually high. From these results, we can deduce that the dye **9** shows the most exhaustion value because this dye has lower molecular weight than others. The low substantivity of acid dye **8** is due to high molecular weight. Although the dye **8** has higher molecular weight than dye **11**, it is more substantivity, due to it contains diazo component.



**Figure 1.** Exhaustion of acid dyes **8-11** on wool at various pH values at 2% o.w.f.

**Table 1.** Exhaustion of acid dyes **8-11** on wool at various pH values.

Comp. No.	Exhaustion (%)				
	pH 3	pH 4	pH 5	pH 6	pH 7
<b>8</b>	80.0	77.0	66.5	41	33.5
<b>9</b>	91.5	88.5	79.5	66	60.0
<b>10</b>	82.0	79.0	68.5	43	35.0
<b>11</b>	75.5	74.0	60.0	37	30.0

#### 4.1.2. Effect of Dye Concentration on Percent of Dyeing Exhaustion

**Figure 2** shows the exhaustion of the dyes on wool using different depth of shades (1% - 5% o.w.f.) at pH 4 and 100°C. Increasing the dye concentration reduces the exhaustion on wool. From these results, we can deduce that the dye **9** exhibits the most exhaustion value while the dye **11** shows the lowest one.

#### 4.1.3. Effect of Dyeing Time on Percent of Dyeing Exhaustion

**Figure 3** indicates the variation of dyeing time with temperature at pH 4 and (2% o.w.f.) dye concentration. It is apparent that the dye-fibre reaction is characterized by fast initial rate followed by slower rate, which levels off within the last 30 min of dyeing process. From these results, we can deduce that the dye **9** shows the most exhaustion value while the dye **11** shows the lowest one.

### 4.2. Dyeing of Coumarin Compounds 8-11 on Silk

#### 4.2.1. Effect of pH on Percent of Dyeing Exhaustion

**Table 2** and **Figure 4** show the effect of pH on the exhaustion of acid dyes on silk fibre. The data revealed that at lower dyeing pH values (pH 5), the substantivity of the acid dyes on silk is virtually high. From these results, we can deduce the acid dye **9** exhibits the most exhaustion value because this dye has lower molecular weight than others. The low substantivity of acid dye **10** is due to high molecular weight, which decreases substantivity. Although the dye **10** has higher molecular weight than dye **11**, it is more substantivity, because it contains diazo component.

#### 4.2.2. Effect of Dye Concentration on Percent of Dyeing Exhaustion

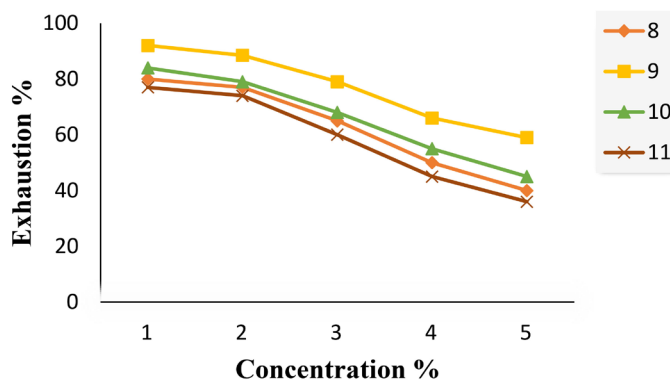
**Figure 5** shows the exhaustion of the dyes on silk using different depth of shades (1% - 5% o.w.f.) at pH 5 and 100°C. Increasing the dye concentration reduces the exhaustion on silk. From these results, we can deduce the dye **9** is the most exhaustion value while the dye **11** is the lowest one.

#### 4.2.3. Effect of Dyeing Time on Percent of Dyeing Exhaustion

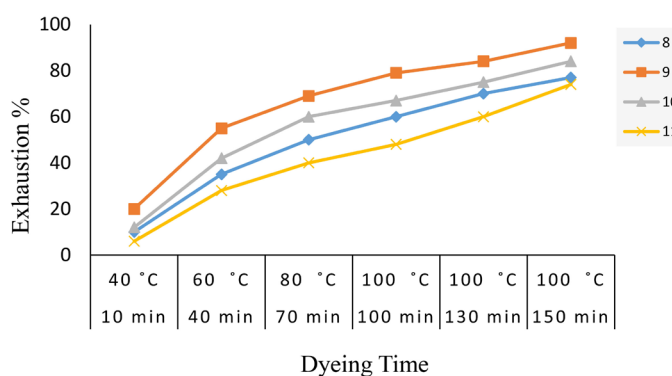
**Figure 6** indicates the variation of dyeing time with temperature at pH 5 and (2% o.w.f.) dye concentration. It is apparent that the dye-fibre reaction is characterized by fast initial rate followed by slower rate, which levels off within the last 30 min of dyeing process. From these results, we can deduce the acid dye **9** shows the most exhaustion value while the dye **11** is the lowest one *i.e.* increasing the time of dying, this leads to the increasing of the exhaustion values.

### 4.3. Colorimetric and Fastness Properties for All Dyeings

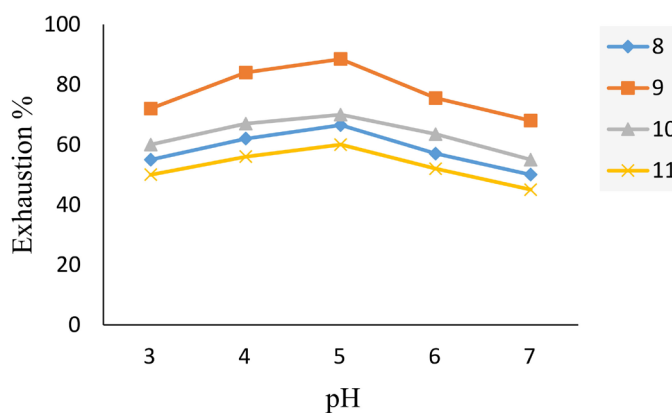
The colorimetric CIE L \* a \* b \* C \* h° data of the dyed wool and silk using the dye are shown in **Table 3**. The colour parameters were evaluated by means of the Cielab system and the modified CIEL \* C \* H° (D65/10°) system. The following colour parameters for the dyed samples were obtained by the digital Cielab system: L\*—lightness, a\*—redness if positive coordinate, or greenness if negative coordinate, b\*—yellowness if positive coordinate, or blueness if negative coordinate, C\*—chromaticity, Ho—hue of the colour, X—coordinate x, Y—coordinate y, Z—coordinate z [32]. As shown in **Table 4**, the fastness to washing, rubbing and perspiration of all samples dyed with the dye was excellent to very good irrespective to the fabric used. Chromatic parameters were determined in comparison for samples dyed with all dyes. The light fastness of the dyes was found to



**Figure 2.** Exhaustion of acid dyes **8-11** on wool at various concentrations at pH 4.



**Figure 3.** Exhaustion of acid dyes **8-11** on wool at pH 4 (2% o.w.f.) with varying of dyeing time.

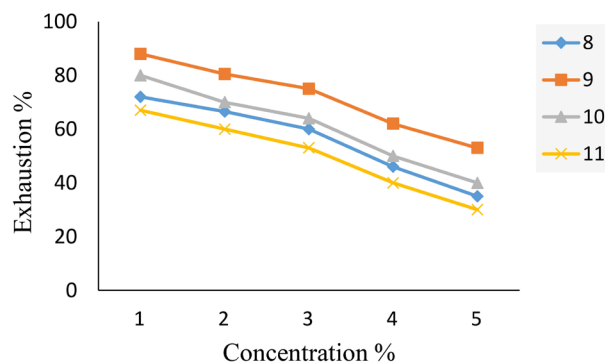


**Figure 4.** Exhaustion of acid dyes **8-11** on silk at various pH values.

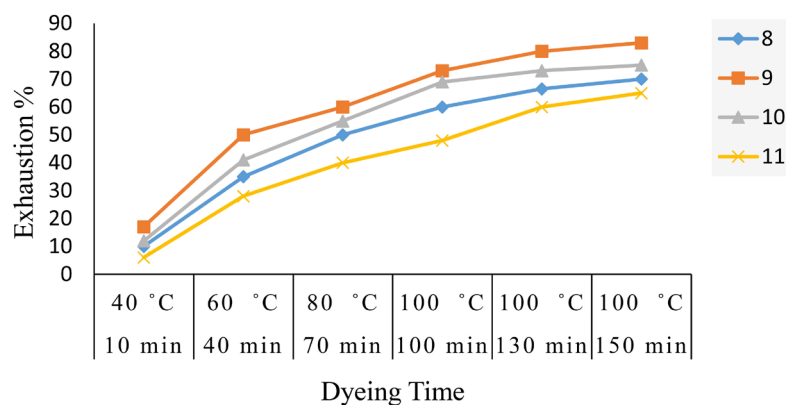
**Table 2.** Exhaustion of acid dyes **8-11** on silk at various pH values.

Comp. No.	Exhaustion (%)				
	pH 3	pH 4	pH 5	pH 6	pH 7
<b>8</b>	55	62	66.5	57.0	50
<b>9</b>	72	84	88.5	75.5	68
<b>10</b>	60	67	70.0	63.5	55
<b>11</b>	50	56	60.0	52.0	45





**Figure 5.** Exhaustion of acid dyes **8-11** on silk at various concentrations at pH 5.



**Figure 6.** Exhaustion of acid dyes **8-11** on silk at pH 5 (2% o.w.f.) with varying of dyeing time.

**Table 3.** Colorimetric data of the dyed wool and silk fabrics using acid dyes **8-11** (2% o.w.f.) at 100°C and at pH 4.

Comp. No.	Fabric	K/S	L*	a*	b*	C*	Ho	E*
<b>8</b>	Wool	22.67	45.81	45.08	54.94	71.06	50.63	84.55
	Silk	4.73	60.13	31.93	51.68	60.74	58.29	85.47
<b>9</b>	Wool	20.71	19.95	2.790	-9.940	10.32	74.32	22.46
	Silk	8.93	30.13	13.81	-8.150	16.03	30.54	34.13
<b>10</b>	Wool	16.20	23.50	12.10	-4.200	12.80	19.14	26.70
	Silk	4.900	34.00	5.800	-10.10	11.64	60.13	35.93
<b>11</b>	Wool	65.11	22.84	24.10	28.75	37.51	50.02	43.92
	Silk	75.10	-1.140	34.89	1.670	34.92	2.740	34.94

K/S: colour strength; L\*: lightness; C\*: chromaticity; Ho: hue of the colour; E\*: total colour; a\*: redness if positive coordinate, or greenness if negative coordinate; b\*: yellowness if positive coordinate, or blueness if negative coordinate.

depend on the mobility of electrons through conjugated system from conjugated system from thiazole ring with coupler compounds afforded a good value of light fastness. The visible absorption spectra of some dyes showed that colours of dyes in the range are blue-purple, in addition, others in range are yellow-brown. The fastness of dyed fabrics to water, washing, alkaline and acid perspirations and rubbing was found to be very high irrespective of degree of sulphonation in the coupling component.

**Table 4.** Fastness properties of dyed wool and silk fabrics using acid dyes **8-11** (2% o.w.f.) at 100°C and at pH 4.

Comp. No.	Fabric	Fastness to Rubbing		Wash Fastness			Fastness to Perspiration						Light Fastness
							Alkaline			Acidic			
		Dry	Wet	Alt	SC	SW	Alt	SC	SW	Alt	SC	SW	
8	Wool	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	Silk	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
9	Wool	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	Silk	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
10	Wool	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	Silk	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
11	Wool	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	Silk	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4

Alt: colour change of dyed sample; SC: staining on cotton; SW: staining on wool, wash-scale (1-5) and light-scale (1-8).

## 5. Conclusion

This article shows that: the synthesis of some novel coumarin compounds is to be used as acid dyes. Dye **9** named sodium 6-(2-(1-cyano-2-oxo-2-(2-oxo-2*H*-chromen-3-yl)ethylidene)hydrazinyl)-4-hydroxynaphthalene-2-sulfonate shows the most exhaustion value on wool and silk fibres.

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