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

Mahmoud S. Bashandy¹,²*, Fatma A. Mohamed³,⁴, Mohamed M. El-Molla³,⁵, Mahmoud B. Sheier¹, Ahmed H. Bedair¹

¹Chemistry Department, Faculty of Science (Boys), Al-Azhar University, Cairo, Egypt
²Chemistry Department, University College in Al-Jamoum, Umm Al-Qura University, Makkah, Saudi Arabia
³Textile Research Division, National Research Centre, Giza, Egypt
⁴Balguenvzh University College, Department of Female Student, Umm Al-Qura University, Makkah, Saudi Arabia
⁵Chemistry Department, College of Sciences & Art, Al Jouf University, El-Quraiat, Saudi Arabia

Received 31 December 2015; accepted 17 March 2016; published 21 March 2016

Copyright © 2016 by authors and Scientific Research Publishing Inc.
This work is licensed under the Creative Commons Attribution International License (CC BY).
http://creativecommons.org/licenses/by/4.0/

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-sulfobenzene-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)benzenesulphonium 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-chromene-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-

*Corresponding author.

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, $^{1}$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 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 3indicated absorption bands at $v_{\text{max}} = 3370$ cm$^{-1}$ for hydroxyl group, 1653 cm$^{-1}$ for carbonyl group and 1456, 1290 cm$^{-1}$ for nitro group. $^{1}$H NMR spectrum showed three singlet signals at $\delta = 8.05, 10.30$ and 11.78 ppm corresponding to 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 ppm for H 2,6 and H 3,5of nitrophenyl ring, respectively, two doublet signals, each doublet for one proton at $\delta = 7.17$ and 8.14 ppm due to H 3 and H 4 of hydroxyphenyl ring, respectively. IR spectrum of compound 4 showed absorption bands at $v_{\text{max}} = 3462$ cm$^{-1}$ for hydroxyl group, $v_{\text{max}} = 1658$ cm$^{-1}$ for carbonyl group and $v_{\text{max}} = 1386, 1150$ cm$^{-1}$ for sulphate group. $^{1}$H NMR spectrum showed three singlet signals at $\delta = 7.19, 10.33$ and 11.56 ppm corresponding to H 6 of hydroxyphenyl-
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-2H-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 $v_{\text{max}} = 2207$ cm$^{-1}$ for cyano group, $v_{\text{max}} = 1703$ and $1636$ 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)-diazenyl)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 $v_{\text{max}} = 3421$ and $3350$ cm$^{-1}$ assignable to 2NH groups, another absorption bands at $v_{\text{max}} = 2212$ cm$^{-1}$ for cyano group and at $v_{\text{max}} = 1755$ and $1657$ 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-2H-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 $v_{\text{max}} = 3424$ and $3320$ cm$^{-1}$ for OH and NH groups, respectively, $v_{\text{max}} = 2248$ cm$^{-1}$ for cyano group and at $v_{\text{max}} = 1710$ and $1632$ cm$^{-1}$ for cyclic carbonyl of coumarin and acyclic carbonyl, respectively.
The 1H NMR spectrum of compound 9 showed two singlet signals at δ = 12.71 and 12.80 ppm corresponding to protons of OH and NH groups. IR spectrum of compound 10 revealed broad absorption band from $v_{\text{max}} = 3486$ to $3380 \text{ cm}^{-1}$ for OH and NH groups, $v_{\text{max}} = 2225 \text{ cm}^{-1}$ for cyano group and at $v_{\text{max}} = 1710$ and 1632 cm$^{-1}$ 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 $v_{\text{max}} = 3325 \text{ cm}^{-1}$ for NH group, $v_{\text{max}} = 1736$ and 1617 cm$^{-1}$ 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 $m/z = 394$. 
Interaction of compound 2 with benzene-1,4-diamine in refluxing ethanol afforded a single product identified as N-(4-aminophenyl)-2-oxo-2H-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 \( v_{\max} = 3458 \) and 3360 cm\(^{-1}\) assignable to amino group, \( v_{\max} = 3320 \) cm\(^{-1}\) for NH group and \( v_{\max} = 1702 \) and 1650 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 \((C_6H_5N^-)\) (Chart 1).

Compounds 12 was suspended with stirring in concentrated sulfuric acid and cooled to 0°C - 5°C then diazotized by adding sodium nitrite. After stirring at 0°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°C to give compound 13 (Scheme 4). IR spectrum of compound 13 revealed broad absorption band from \( v_{\max} = 3505 \) to 3273 cm\(^{-1}\) for hydroxyl, amino and NH groups and at \( v_{\max} = 1700 \) and 1648 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 \( N-(4′-amino-3,3′-dimethoxy-[1,1′-biphenyl]-4-yl)-2-oxo-2H-chromene-3-carboxamide \) (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 \( v_{\max} = 3400 \) to 3270 cm\(^{-1}\) due to amino and NH groups and \( v_{\max} = 1718 \) and 1658 cm\(^{-1}\) for two carbonyl groups of coumarin ring and amide group, respectively. Besides, the mass spectrum was compatible with the molecular formula \( C_{23}H_{20}N_2O_5 \), \( m/z =416 \) 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 \( v_{\max} = 3509 \) to 3380 cm\(^{-1}\) due to hydroxyl, amino and NH groups, \( v_{\max} = 1726 \) and 1661 cm\(^{-1}\) for two carbonyl groups of coumarin ring and amide group, respectively and \( v_{\max} = 1449 \) 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, di-ethyl malonate and/or malononitrile afforded derivatives of 3-acetyl-2-oxo-2H-chromene-3-carboxylate17 and 2-imino-2H-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 \( v_{\max} = 1745 \) and 1676 cm\(^{-1}\) for two carboxyl groups of coumarin ring and acetyl group, respectively, \( v_{\max} = 1522 \) cm\(^{-1}\) corresponding to N=N group and two absorption bands at \( v_{\max} = 1338 \) and 1231 cm\(^{-1}\) for nitro group. 1H NMR spectrum of 16 revealed three singlet signals at \( \delta = 2.53, 8.42 \) and 8.80 ppm for methyl, \( H_2 \) and \( H_1 \) of coumarin, respectively, two doublet signals each doublet signal for one proton at \( \delta = 7.65, 8.25 \) 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 ppm corresponding to \( H_{2,6} \) and \( H_{3,5} \) of nitrophenyl ring, respectively. IR spectrum of compound 17 revealed absorption bands at \( v_{\max} = 1741 \) and 1705 cm\(^{-1}\) for two carbonyl groups of coumarin ring and ester group, respectively, \( v_{\max} = 1521 \) cm\(^{-1}\) corresponding to N=N group and two absorption bands at \( v_{\max} = 1338 \) and 1251 cm\(^{-1}\) for nitro group. 1H NMR spectrum of 17 revealed triplet and quartet signals at \( \delta = 1.30 \) and 4.30 ppm, respectively corresponding to protons of methyl and methylene of ester group, respectively, two singlet signals at \( \delta = 8.40 \) and 8.89 ppm for \( H_2 \) and \( H_4 \) of coumarin, respectively, two doublet signals each doublet signal for one proton at \( \delta = 7.60, 8.19 \) ppm corresponding to \( H_6 \) and \( H_7 \) of coumarin, respectively, besides two doublet signals each doublet signal for two protons at \( \delta = 8.03 \) and 8.52 ppm corresponding to \( H_{2,6} \) and \( H_{3,5} \) of nitrophenyl ring, respectively.

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

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_10H_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 v_max = 1754 and 1672 cm^{-1} for two carbonyl groups of coumarin ring and acetyl group, respectively, v_max = 1564 cm^{-1} corresponding to N=N group and two absorption bands at v_max = 1382 and 1122 cm^{-1} for SO_2 group. ^1H NMR spectrum of 19 revealed triplet signal at δ = 2.57 ppm corresponding to protons of methyl group, two singlet signals at δ = 8.19 and 8.80 ppm for H_5 and H_4 of coumarin, respectively, two doublet signals each...
doublet signal for one proton at $\delta = 7.62, 7.85$ ppm corresponding to H$_8$ and H$_7$ of coumarin, respectively, besides two doublet signals each doublet signal for two protons at $\delta = 7.78$ and 8.52 ppm corresponding to H$_2$ and H$_3$ of benzenesulfonate ring, respectively.

IR spectrum of compound 20 revealed an absorption broad band at $v_{\text{max}} = 3384$ for OH groups, $v_{\text{max}} = 1486$ cm$^{-1}$ corresponding to N=N group and two absorption bands at $v_{\text{max}} = 1384$ and 1132 cm$^{-1}$ for SO$_2$ group. Mass spectrum of compound 20 showed a molecular ion peak at m/z = 552 (M$^+\text{-}2\text{N}_2$) and showed other peaks at m/z = 450 corresponding to fragment ($C_{20}H_{15}N_6O_5S^+$) and m/z = 295 for fragment ($C_{14}H_{10}N_6O_2^+$) (Chart 3).

3. Experimental

3.1. Methods and Materials

3.1.1. Wool Fabric
Wool fabric of 310 g/m$^2$, 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$^2$ 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.](image-url)
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 (ν, 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 (DMSO-d₆) were recorded at 400 MHz on a Varian Gemini NMR spectrometer (δ, 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 ±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, cm⁻¹): νmax = 3370 (OH), 1653 (C=O), 1578 (C=C), 1526 (N=N), 1456, 1290 cm⁻¹ (NO₂). ¹H NMR (DMSO-d₆): δ = 7.17 (1H, d, Ar-H₃), 7.95 (2H, d, nitrophenyl-H₂,6), 8.05 (1H, s, Ar-H₆), 8.14 (1H, d, Ar-H₄), 8.32 (2H, d, nitrophenyl-H₃,5), 10.30 ppm (1H, s, OH), 11.78 (1H, s, CHO). Anal. Calcd. for C₁₃H₉N₃O₄ (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, cm⁻¹): νmax = 3462 (OH), 1658 (C=O), 1558 (C=C), 1478 (N=N), 1386, 1150 cm⁻¹ (SO₂). ¹H NMR (DMSO-d₆): δ = 7.17 (1H, d, Ar-H₃), 7.95 (2H, d, nitrophenyl-H₂,6), 8.05 (1H, s, Ar-H₆), 8.14 (1H, d, Ar-H₄), 8.32 (2H, d, nitrophenyl-H₃,5), 10.30 ppm (1H, s, OH), 11.78 (1H, s, CHO). Anal. Calcd. for C₁₃H₉N₂NaO₅S (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, cm⁻¹): νmax = 2931 (CH-aliphatic), 2207 (C≡N), 1703

3.2.8. Sodium 2-{(1-Cyano-2-Oxo-2-{(1-(2-oxo-2H-Chromen-3-yl)Ethylidene)Hydrazinyl)}Ethylidene)Hydrazinyl}-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-4-((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/acetic acid to give 8. Orange crystals, yield, 82%; mp >300˚C.

λ _max (H2O) 518 nm. IR (KBr, cm⁻¹): v _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_{7}Na_{2}O_{9}S_{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 products9and 10, respectively.

1) Sodium 6-{(1-cyano-2-oxo-2-{(2-o xo-2H-Chromen-3-yl)ethylidene)hydrazinyl)-4-hydroxynaphthalene-2-sulfonate (9)

Violet crystals, yield, 88%; mp >300˚C (DMF/acetone), λ _max(H2O) 545 nm. IR (KBr, cm⁻¹): v _max = 3424(OH), 3320 (NH), 2907 (CH-aliphatic), 2248 (C≡N), 1710 (O-C=O), 1632 cm⁻¹ (C=O). 1H NMR (DMSO-d6): δ = 7.22 - 8.81 (10H, m, 2Ar -H + coumarin -H4-8), 12.71, 12.80 ppm (2H, 2s, OH, NH). Anal. Calcd. for C_{22}H_{12}N_{3}NaO_{7}S (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-{(1-cyano-2-oxo-2-{(2-o xo-2H-Chromen-3-yl)ethylidene)hydrazinyl)-5-hydroxynaphthalene-2,7-disulfonate (10)

Violet crystals, yield, 88%; mp >300˚C (DMF/acetone), λ _max(H2O) 520 nm. IR (KBr, cm⁻¹): v _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_{3}Na_{2}O_{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%.
Brownish-yellow crystals, yield, 70%; mp 110°C - 112°C (DMF/acetone). IR (KBr, cm⁻¹): \( ν_{max} = 3400-3270 \) (NH₂, NH), 3183 (CH-aromatic), 2935 (CH-aliphatic), 1718 (O-C=O), 1658 cm⁻¹ (C=O). MS m/z (%): 416 [M⁺] (1), 244 (74), 201 (100), 186 (35), 158 (36). Anal. Calcd. for C_{26}H_{26}N_{2}O_{2} (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-2h-Chromene-3-Carboxamido)Phenyl}-Diazene

Compounds 12 (2.80 g, 0.01 mol) was suspended with stirring in concentrated H₂SO₄ (3 mL) and cooled to 0°C - 5°C then diazotized by adding NaNO₂ (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 HNO₂. There were a colour change from white to brown, sulfamic acid was added to destroy excess HNO₂. 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 0-5°C and maintaining pH 4 by adding AcONa. After stirring for 1 h at 0°C, the diest dye was collected by filtration then recrystallized from DMF/acetone. Violet crystals, yield, 89%; mp >300°C, the dissert dye was checked with starch paper for the presence of HNO₂.

3.2.12. Sodium 4-Amino-3-{(3,3’-Dimethoxy-4’-(2-Oxo-2h-Chromene-3-Carboxamido)Phenyl)Diazene}-5-Hydroxynaphthalene-2,7-Disulfonate

Compounds 14 (4.16 g, 0.01 mol) was suspended with stirring in concentrated H₂SO₄ (3 mL) and cooled to 0°C - 5°C then diazotized by adding NaNO₂ (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 HNO₂. There were a colour change from white to brown, sulfamic acid was added to destroy excess HNO₂. 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 diest dye 15 was collected by filtration then recrystallized from DMF/acetone. Violet crystals, yield, 89%; mp >300°C, \( λ_{max}(H_2O) \) 405 nm. IR (KBr, cm⁻¹): \( ν_{max} = 3505 - 3273 \) (OH, NH₂, NH), 3073 (CH-aromatic), 1700 (O-C=O), 1648 (C=O), 1502 cm⁻¹ (N=N). MS m/z (%): 791 [M⁺+1] (5), 744 (8), 472 (9), 146 (52), 118 (63), 64 (100). Anal. Calcd. for C_{34}H_{24}N_{4}Na_{2}O_{12}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)diazeyl)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)diazeyl)-2h-chromen-2-one

Brown crystals, yield, 59%; mp 225-227°C (DMF).IR (KBr, cm⁻¹): \( ν_{max} = 3050 \) (CH-aromatic), 2928 (CH-aliphatic), 1745 (O-C=O), 1676 (C=O), 1600 (C=C), 1522 (N=N), 1338, 1231 cm⁻¹ (NO₂). \(^1\)H NMR (DMSO-d₆): \( δ = 2.53 \) (3H, s, CH₃), 7.65 (1H, d, coumarin-H₃), 8.08 (2H, d, nitrophenyl-H₂,6), 8.25 (1H, d, coumarin-H₂), 8.42 (1H, s, coumarin-H₂), 8.59 (2H, d, nitrophenyl-H₂,3), 8.80 ppm (1H, s, coumarin-H₂). Anal. Calcd. for C_{17}H_{11}N_{3}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)diazeyl)-2-o xo-2h-chromene-3-carboxylate

Brown crystals, yield, 56%; mp 245°C - 246°C (DMF). IR (KBr, cm⁻¹): \( ν_{max} = 3097 \) (CH-aromatic), 2960 (CH-aliphatic), 1741 (coumarin C=O), 1705 (ester C=O), 1521 (N=N), 1338, 1251 cm⁻¹ (NO₂). \(^1\)H NMR (DMSO-d₆): \( δ = 1.30 \) (3H, t, CH₃), 4.30 (2H, q, CH₂), 7.60 (1H, d, coumarin-H₂), 8.03 (2H, d, nitrophenyl-H₂,6), 8.19 (1H, d, coumarin-H₂), 8.40 (1H, s, coumarin-H₂), 8.52 (2H, d, nitrophenyl-H₂,3), 8.89 ppm (1H, s, coumarin-H₂). Anal. Calcd. for C_{18}H_{13}N_{3}O_{6} (367.31): C, 58.86; H, 3.57; N, 11.44. Found: C, 60.01; H, 3.34; N, 11.68%.
3.2.14. Sodium 4-((3-Acetyl-2-Oxo-2h-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, cm\(^{-1}\)): \(\nu_{\text{max}} = 3058 (\text{CH-aromatic}), 2922 (\text{CH-aliphatic}), 1754 (\text{O=C=O}), 1672 (\text{C=O}), 1620 (\text{C=C}), 1564 (\text{N=N}), 1382, 1122 \text{ cm}^{-1} (\text{SO}_2)\). \(^1\)H NMR (DMSO-d\(_6\)): \(\delta = 2.57 (3\text{H, t, CH}_3), 7.62 (1\text{H, d, coum a-rin-H8}), 7.78 (2\text{H, d, Ar -H2,6}), 7.85 (1\text{H, d, coumarin- H7}), 8.19 (1\text{H, s, coumarin- H5}), 8.52 (2\text{H, d, Ar -H3,5}), 8.80 ppm (1\text{H, s, coumarin-H4})\). Anal. Calcd. for C\(_{17}\)H\(_{11}\)N\(_2\)NaO\(_6\)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-Diyldenedi(Methanylylidene))Bis(4-Hydroxy-3,1-Phenyl-Ene))Bis(Diazene-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, cm\(^{-1}\)): \(\nu_{\text{max}} = 3384 (\text{OH}), 3108 (\text{CH -aromatic}), 2934 (\text{CH-aliphatic}), 2934 (\text{CH-aliphatic}), 1600 (\text{C=O}), 1486 (\text{N=N}), 1384, 1132 \text{ cm}^{-1} (\text{SO}_2)\). MS m/z (%): 552 [M\(^-2\text{N}_2\)] (60), 450 [C\(_{20}\)H\(_{13}\)N\(_5\)O\(_8\)S\(_2\)] (58), 295 [C\(_{14}\)H\(_{10}\)N\(_6\)O\(_7\)^+] (58), 80 (100) (Chart 3). Anal. Calcd. for C\(_{20}\)H\(_{20}\)N\(_6\)O\(_8\)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 substantive, 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.](image-url)
Table 1. Exhaustion of acid dyes 8-11 on wool at various pH values.

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>pH 3</th>
<th>pH 4</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>80.0</td>
<td>77.0</td>
<td>66.5</td>
<td>41</td>
<td>33.5</td>
</tr>
<tr>
<td>9</td>
<td>91.5</td>
<td>88.5</td>
<td>79.5</td>
<td>66</td>
<td>60.0</td>
</tr>
<tr>
<td>10</td>
<td>82.0</td>
<td>79.0</td>
<td>68.5</td>
<td>43</td>
<td>35.0</td>
</tr>
<tr>
<td>11</td>
<td>75.5</td>
<td>74.0</td>
<td>60.0</td>
<td>37</td>
<td>30.0</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>pH 3</th>
<th>pH 4</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>55</td>
<td>62</td>
<td>66.5</td>
<td>57.0</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>72</td>
<td>84</td>
<td>88.5</td>
<td>75.5</td>
<td>68</td>
</tr>
<tr>
<td>10</td>
<td>60</td>
<td>67</td>
<td>70.0</td>
<td>63.5</td>
<td>55</td>
</tr>
<tr>
<td>11</td>
<td>50</td>
<td>56</td>
<td>60.0</td>
<td>52.0</td>
<td>45</td>
</tr>
</tbody>
</table>
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.

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

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.

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Fabric</th>
<th>Fastness to Rubbing</th>
<th>Wash Fastness</th>
<th>Fastness to Perspiration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Dry</td>
<td>Wet</td>
<td>Alt</td>
</tr>
<tr>
<td>8</td>
<td>Wool</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td>Silk</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>9</td>
<td>Wool</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td>Silk</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>10</td>
<td>Wool</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td>Silk</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>11</td>
<td>Wool</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td>Silk</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
</tr>
</tbody>
</table>

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-2H-chromen-3-yl)ethylidene)hydrazinyl)-4-hydroxynaphthalene-2-sulfonate shows the most exhaustion value on wool and silk fibres.

References


http://dx.doi.org/10.1016/j.saa.2015.06.024


