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Research Article

Design, Synthesis, and Evaluation of Dyeing Properties of 7-Hydroxy-4-Substituted Coumarin Dyes

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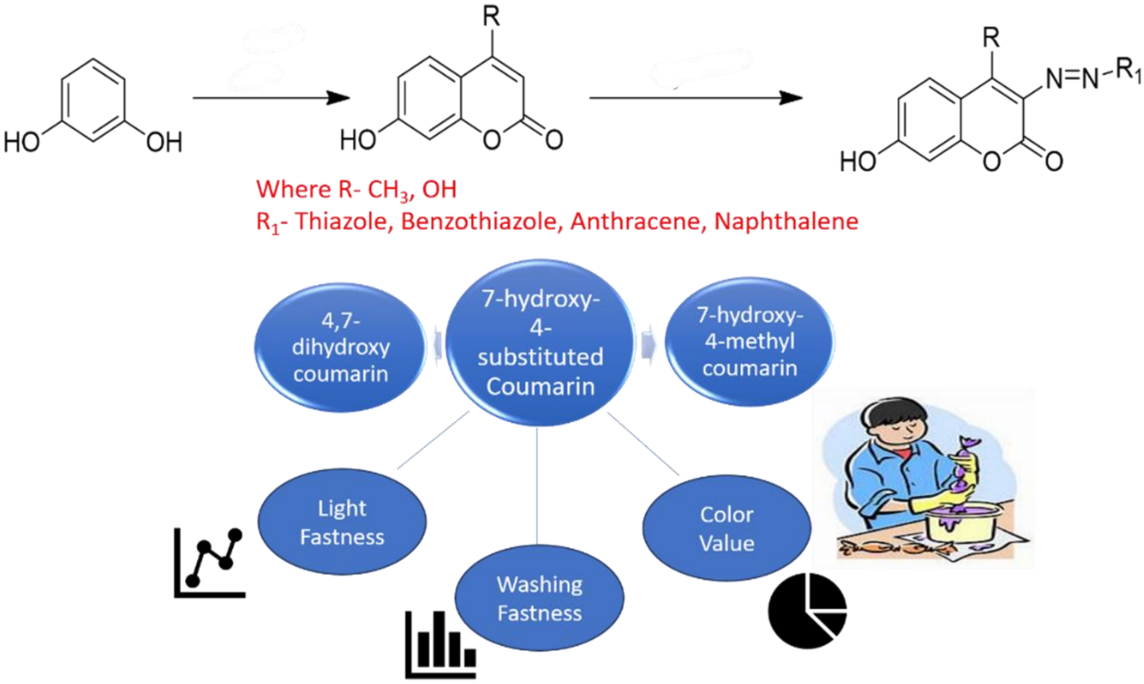
Graphical Abstract



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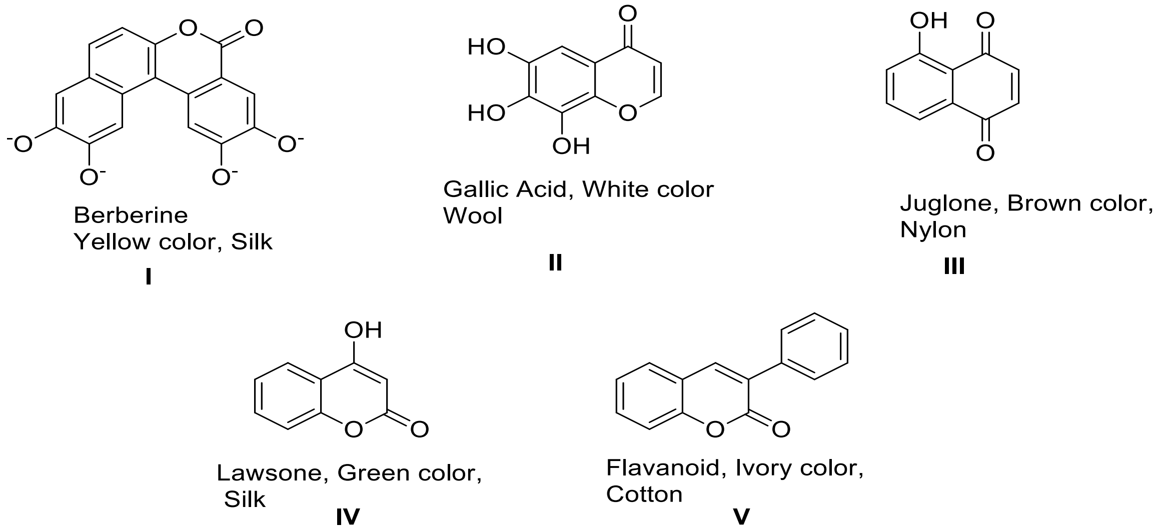
ABSTRACT

The study focuses on the synthesis, characterization, and performance evaluation of a series of coumarin-based dyes, specifically 3-(thiazole/benzothiazole/naphthalene/anthracene)-7-hydroxy-4-substituted-2H-chromen-2-one derivatives (1, 3, 2a-d, 4a-d). These compounds were synthesized and thoroughly characterized using 1H NMR, 13C NMR, IR spectroscopy, and HRMS. The synthesized dyes were tested for their ability to dye various fabrics, including cotton, polyester, and wool. The dyes demonstrated a range of color strengths on polyester fabric, with some showing exceptional dyeing performance. The color values for the dyes on polyester were found on dyes (1, 2a-d) 1.00, 1.02, 3.55, 2.01, 1.55, and dyes (3, 4a-d) 1.59, 2.02, 2.25, 5.55. These results indicate that the synthesized dyes generally provided good to excellent dyeing performance on polyester, outperforming methyl orange, a common reference dye. The dyes were also evaluated for light fastness, sublimation resistance, and perspiration resistance on the fabrics. The results showed that the dyes exhibited moderate to excellent performance in durability and color retention under various conditions. These dyes were further evaluated for their antibacterial and water-testing properties. These results were compared for the dye solutions before and after the dyeing process, helping to evaluate the environmental consequences of using these dyes.

Keywords: Coumarin, IR, NMR, HRMS, Dyeing, Antibacterial.

1. Introduction

Coumarins, a significant class of naturally occurring compounds, were first identified by Vogel in 1822 from tonka beans (Fabaceae family), with the name "Coumarou" deriving from French. These compounds are prevalent in the plant kingdom and have been synthetically produced for commercial use for many years [1]. Due to their strong fluorescence and high quantum yield [2-6], coumarin-based dyes are employed as fluorescent chemosensors in fields such as molecular imaging, bioinorganic chemistry, and analytical chemistry. The introduction of different functional groups, such as methyl, amino, hydroxy, or methoxy, at the 4th or 7th position of coumarin derivatives alters their fluorescence properties, leading to changes in their absorption and emission characteristics [7-9]. Compounds like 7-hydroxy-4-substituted coumarins have been utilized to develop optical brighteners [10] and disperse azo dyes for textile dyeing [11]. Various primary phytochemicals that contain coumarin structures are illustrated in **Figure 1 (I-V)**, which are responsible for the diverse colors of fabrics.



Berberine
Yellow color, Silk
I

Gallic Acid, White color
Wool
II

Juglone, Brown color,
Nylon
III

Lawsone, Green color,
Silk
IV

Flavanoid, Ivory color,
Cotton
V

Figure 1 Structure of Coumarin-Based Fabric Dyes

Dyes **(I-V)** can have numerous carcinogenic effects on the human body [12]. These dyes **(I-V)** exhibit poor fastness properties, including low perspiration and light fastness. Due to inadequate perspiration fastness, they can lead to various allergic reactions and skin irritations, such as eye irritation, shock, increased heart rate, and vomiting. Additionally, the dispersed dyes currently available on the market contribute significantly to water pollution. As a result, researchers are primarily focused on developing skin-safe and environmentally friendly dyes that do not require the use of any mordants. Coumarin compounds are often considered safer and more eco-friendly compared to synthetic ones; however, their higher cost and complex application process make them impractical for many commercial uses [13]. One key challenge is that compound sources typically contain only around 3% of the active dyeing compounds, necessitating significant amounts of raw materials for processing [14]. This factor significantly raises production costs and limits the feasibility of natural dyes for large-scale manufacturing. Existing azo dyes supplanted natural ones due to their broader color range, affordability, and greater resistance to fading from sunlight, water, and chemicals [15]. By the late 20th century, over 12,000 synthetic dyes had been created. However, about 15% of these synthetic dyes are released into the environment, leading to serious environmental issues. This pollution can block sunlight from penetrating water bodies and disrupt photosynthesis by depleting oxygen levels and leading to aquatic life, plant death, and reduced growth of animal populations [16].

This paper aims to develop coumarin-based dyes combined with heterocyclic units such as thiazole, benzothiazole, naphthalene, and anthracene, specifically 3-(thiazole/ benzothiazole/ naphthalene/ anthracene)-7-hydroxy-4-substituted-2*H*-chromen-2-one, which have a less detrimental environmental impact. Note: 2-Naphthylamine is classified as a human carcinogen, with several reports documenting cases of bladder cancer among workers in France due to exposure to 2-naphthylamine [5]. The main goal of this research is to devise a more efficient and cost-effective method for synthesizing 7-hydroxy-4-substituted coumarins, thus enabling their large-scale industrial production.

This paper presents the synthesis and characterization of a series of coumarin-based compounds, including **(1, 3, 2a-d, 4a-d)**.

2. Material and Methods

2.1 Chemicals & Reagents

The chemicals and solvents utilized in this study were of analytical grades (AR) and sourced from Sigma-Aldrich and Spectrochem with 96% purity. The melting points of the compounds were determined using an open capillary melting point apparatus. Infrared (IR) spectroscopic analysis was performed using a Shimadzu IR Affinity Fourier-Transform Infrared (FTIR) spectrophotometer with KBr discs, and the values are expressed in cm^{-1}. Nuclear Magnetic Resonance (NMR) spectroscopy was conducted using a Bruker Advance NMR spectrophotometer to record the ^1H and ^{13}C NMR spectra. HRMS is detected on XEVO-G3-XS-QTOF. Elemental analysis was performed using a C, H, and N Elemental Analyzer (Elementary Vario EI III Carlo Erba 1108).

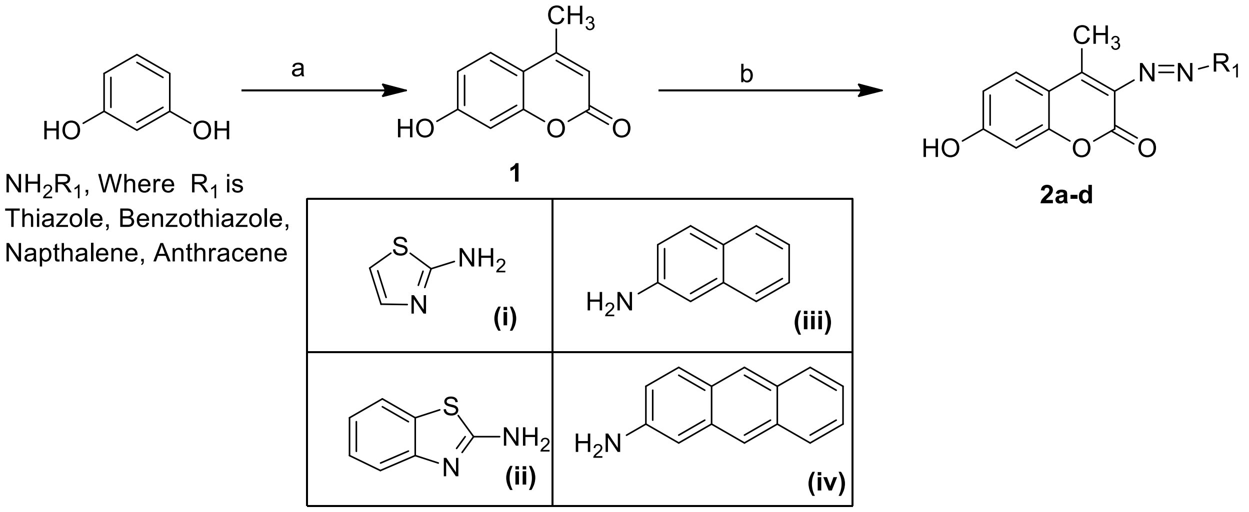
2.2 Standard protocols for synthesis of 3-(thiazole/ benzothiazole/ naphthalene/ anthracene)-7-hydroxy-4-methyl -2*H*-chromen-2-one (2a-d)

2.2.1 Synthesis of 7-hydroxy-4-methyl-2*H*-chromen-2-one (1)

A solution was prepared by combining resorcinol (2 mmol, 0.22 g), ethyl acetoacetate (3 mmol, 0.32 mL), and sulfuric acid (20 mL). The reaction mixture was then stirred for 90 minutes and poured into ice-cold water. The resulting residue was washed repeatedly with water, yielding a crude sample. This sample was crystallized using ethanol, affording the desired compound, 7-hydroxy-4-methyl coumarin **(1)**, with a yield of 95% [6].

2.2.2 Synthesis of 3-(thiazole/ benzothiazole/ naphthalene/ anthracene)-7-hydroxy-4-methyl -2*H*-chromen-2-one (2a-d)

A stirred solution of aromatic amines, namely amino thiazole **(i)**, amino benzothiazole **(ii)**, amino naphthalene **(iii)**, and amino anthracene **(iv)** (10 mmol) in HCl, was cooled to 0-5 °C. A cold solution of $NaNO_2$ (7 mL, 10% w/w) was then added, and the mixture was stirred for 15 minutes to form diazonium salts. After 35 minutes of agitation at 0-5 °C, the cooled diazotized mixture was added to a solution of 7-hydroxy-4-methyl-2*H*-chromen-2-one **(1)** (10 mmol) in 15 mL of NaOH. The resulting mixture was agitated for 30 minutes and then neutralized with 15 mL HCl. The precipitated product was filtered, washed with water, and further purified by recrystallization using ethanol, yielding the desired compounds **(2a-d) (Scheme 1, Figure 2)** [7].



Scheme 1: Reagents & Conditions: (a) ethylacetoacetate, conc. H_2SO_4, 5 °C, 90 mins (b) HCl, $NaNO_2$,0 °C, 45 mins, R_1-NH_2, conc.HCl, NaOH, 0 °C, 30 mins

Figure 2 Synthesis of 3-(thiazole/ benzothiazole/ naphthalene/ anthracene)-7-hydroxy-4-methyl-2*H*-chromen-2-one

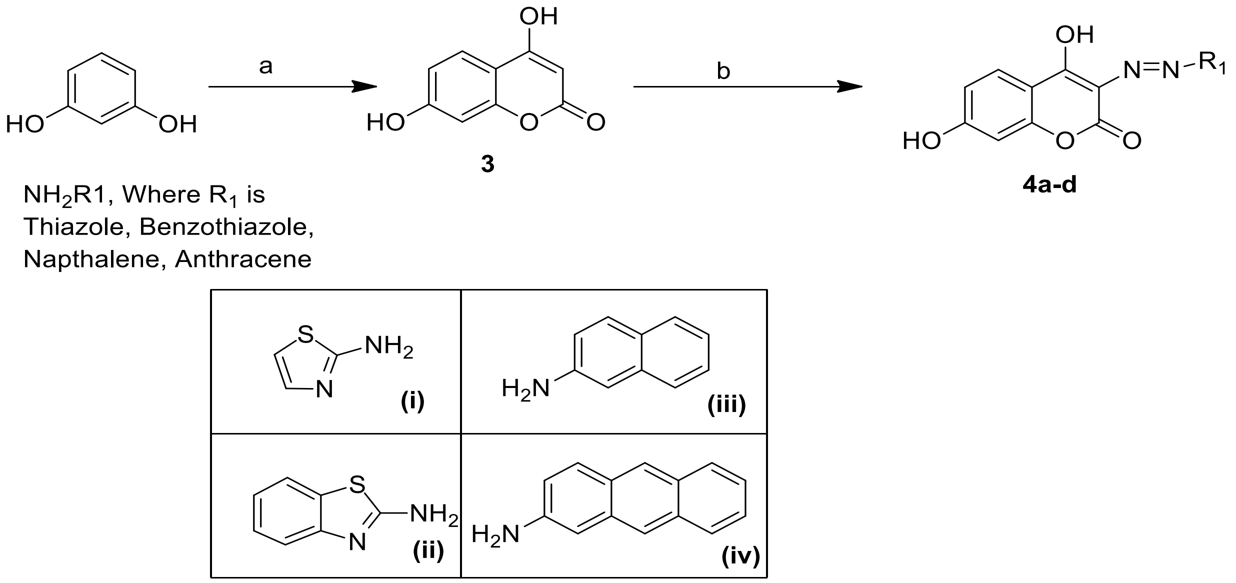
2.2.3 Standard protocols for synthesis of 3-(thiazole/ benzothiazole/ naphthalene/ anthracene)-4,7-dihydroxy-2*H*-chromen-2-one (4a-d)

2.3.1 Synthesis of 4,7-dihydroxy-2*H*-chromen-2-one (3)

A mixture of resorcinol (11 mmol, 2.0 eq.), malonic acid (1.2 g, 11 mmol, 1.0 eq.), zinc chloride (3.53 g, 33 mmol, 2 eq.), and phosphorus oxychloride (3.18 mL, 33 mmol, 2 eq.) was stirred at 70°C for 24 hours. The resulting precipitate was filtered, washed repeatedly with water, and dissolved in sodium hydroxide. The insoluble suspension was removed by filtration, and the filtrate was acidified with concentrated hydrochloric acid. The precipitate formed was collected by filtration, and the crude compound was crystallized from methanol to yield the desired product with a 75% yield, as shown in **Figure 3, Scheme 2** [8].

2.3.2 Diazotization of 4,7-dihydroxy-2*H*-chromen-2-one

An ice-cold solution of aromatic amine (5 mmol) in 3N HCl (15 mL) was stirred, and a cold solution of $NaNO_2$ (3.5 mL, 15 wt.%) was added. The mixture was stirred for 35 minutes at 0-5 °C to form the diazonium salt. A solution of 4,7-dihydroxy coumarin (5 mmol) in 5 wt.% aqueous NaOH (7 mL) was vigorously stirred into the cold diazonium solution. The mixture was stirred for 30 minutes and then neutralized with 10 wt.% HCl (15 mL). The resulting precipitate was filtered, washed with water, and recrystallized from ethanol to yield the desired product [9].

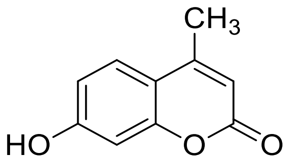


Scheme 2: Reagents & Conditions: (a) Malonic acid, Zinc Chloride, Phosphorus Oxychloride, 24 hrs, 70,°C (b) HCl, $NaNO_2$, 0 °C, 45 mins, R_1-NH_2, conc.HCl, NaOH, 0 °C, 30 mins

Figure 3 Synthesis of 3-(thiazole/ benzothiazole/ naphthalene/ anthracene)-4,7-dihydroxy-2*H*-chromen-2-one

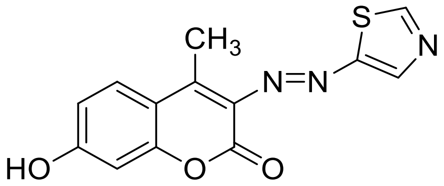
2.4 Spectral Analysis of 7-hydroxy-4-substituted coumarin (1, 3, 2a-d, 4a-d)

7-hydroxy-4-methyl-2*H*-chromen-2-one (1)



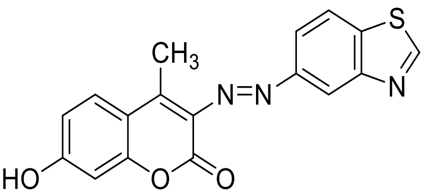
Pale Yellow (Powder), $C_{10}H_8O_3$, 175-190°C, IR (KBr, cm^{-1}): 1656 (C-H), 1678 (C=C), 3340 (O-H), 1270 (C-O); ^{1}H NMR ($CDCl_3$) δ 2.04 (s, CH_3), 4.19 (s, OH), 5.69 (s, 1H), 6.46 (d, 1H, 2.2 Hz), 7.09 (d, 1H), 7.24 (d, 1H); ^{13}C NMR (125 MHz, DMSO-d^6) δ 160.1 (C_2), 158.5 (C_7), 130.4 (C_8), 154.1 (C_9), 152.7 (C_4), 126.8 (C_5), 112.6 (C_6), 112.5 (C_3), 112.3 (C_{10}), 20.1 (CH_3); [M+H+] with m/z 177.0224, 176.0534; CHN: Calc. C, 68.12; H, 4.65. Found: C, 68; H, 4.5.

4-methyl-7-hydroxy-3-(thiazole-5-yldiazenyl)-2*H*-chromen-2-one (2a)



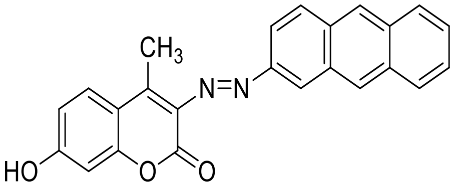
Black (Powder), $C_{13}H_9N_3O_3S$, check molecular formula as per structure H9. 190-195°C, IR (KBr, cm^{-1}): 1650 (C-H), 1675 (C=C), 3240 (O-H), 1280 (C-O), 2263(N=N), 2527 (S-H), 1680 (C=N); ^{1}H NMR ($CDCl_3$) δ 2.57 (s, CH_3), 5.40 (s, OH), 6.59 (s, 1H), 6.7 (d, 1H), 7.6 (d, 1H), 8.2 (d, 1H), 9.2 (d, 1H); ^{13}C-NMR (125 MHz, DMSO-d^6) δ 158.2 (C_7), 155.6 (C_2), 154.5 (C_9), 152.5 (C_4), 148.7 (C_{13}), 136.3 (C_{11}), 126.2 (C_5), 124.5, 121.6 (C_{12}), 121.8 (C_6), 113.4 (C_{10}), 111.5 (C_3), 102.3 (C_8), 18.8 (CH_3); [M+H+] with m/z 288.1545; CHN: Calc. C, 54.5; H, 3.4; N, 15.2; S, 12.0; Found: C, 54.2; H, 3.23; N, 14.7; S, 12.4.

3-(benzothiazole-5-yldiazenyl)-7-hydroxy-4-methyl-2*H*-chromen-2-one (2b)



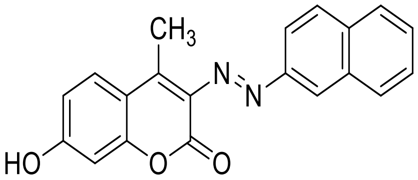
Light Orange (Powder), $C_{17}H_{11}N_3O_3S$, 250-270°C, IR (KBr, cm^{-1}): 1654 (C-H), 1680 (C=C), 3420 (O-H), 1290 (C-O), 2173(N=N), 2620 (S-H), 1680 (C=N); ^{1}H NMR ($CDCL_3$)9 signals should be present δ 2.47 (s, CH_3), 5.40 (s, OH), 6.25 (s, 1H), 6.4 (d, 1H), 6.7 (dd, 2H), 7.0 (d, 1H), 8.1 (dd, 2H), 8.2 (dd, 2H), 4.25(d, 1H); ^{13}C NMR (125 MHz, DMSO-d^6) δ 159.6 (C_{11}),155.7 (C_7), 155.6 (C_9), 152.6 (C_2), 148.8 (C_4), 136.4 (C_{12}), 126.2 (C_{15}), 124.7 (C_{14}), 121.5 (C_{17}), 121.9 (C_{13}), 113.5 (C_{16}), 112.8 (C_5), 107.9 (C_{10}), 102.0 (C_8), 107.7 (C_3), 112.4 (C_6), 103.4 (C_8), 18.5 (CH_3); [M+H+] with m/z 388.2474; CHN: Calc. C, 61.4; H, 3.5; N, 14.8; S, 9.6. Found: C, 61.2; H, 3.4; N, 13.2; S, 9.6.

3-(anthracene-2-yldiazenyl)-7-hydroxy-4-methyl-2*H*-chromen-2-one (2c)



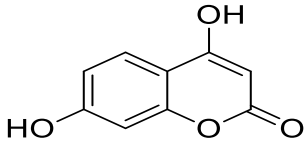
Grey (Powder), $C_{24}H_{16}N_2O_3$, 300-310°C, IR (KBr, cm^{-1}): 1660 (C-H), 1675 (C=C), 3350 (O-H), 2164 (N=N); ^{1}H NMR ($CDCl_3$) δ 2.47 (s, CH_3), 5.23 (s, OH), 6.53 (d, 1H), 6.7 (d, 1H), 7.4 (d, 1H), 8.19 (dd, 3H), 8.4 (d, 1H), 9.21 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d^6) δ 158.4 (C_7), 155.6 (C_2), 155.8 (C_9), 152.4 (C_4), 131.6 (C_{15}), 129.2 (C_{20}), 128.9 (C_{23}), 126.6 (C_{16}), 126.2 (C_{17}), 125.3 (C_{18}), 126.2 (C_5) 131.8 (C_{13}), 112.8 (C_{10}), 113.7 (C_6), 107.9 (C_3), 102.0 (C_8), 125.3 (C_{11}), 126.0 (C_{12}), 126.5 (C_{14}), 128.1 (C_{19}), 126.5 (C_{21}), 131.7 (C_{22}), 19.4 (CH_3), 131.8 (C_{24}); [M+H+] with m/z 382.1467, CHN: Calc. C, 74; H, 4.6; N, 9.0; Found: C, 73.3; H, 4.3; N, 8.9.

3-(naphthalen-2-yldiazenyl)-7-hydroxy-4-methyl-2*H*-chromen-2-one (2d)



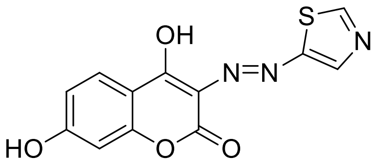
Green (Powder), $C_{20}H_{14}H_2O_{3,}$ 270-290°C, IR (KBr, cm^{-1}): 1654 (C-H), 1680 (C=C), 3320 (O-H), 2173(N=N); ^{1}H NMR ($CDCl_3$) δ 2.48 (s, CH_3), 5.27 (s, OH), 6.50 (d, 1H), 6.61 (d, 1H), 7.1 (d, 1H), 7.4 (dd, 2H), 8.4 (d, 3H), ^{13}C NMR (125 MHz, DMSO-d^6) δ 158.6 (C_7), 155.2 (C_9), 154.3 (C_{13}), 152.7 (C_4), 131.8 (C_{19}), 129.6 (C_{14}), 128.4 (C_{15}), 113.8 (C_{18}), 107.5 (C_3), 112.4 (C_6), 107.9 (C_8), 18.2 (CH_3), 156.1 (C_2), 113.6 (C_{10}), 125.2 (C_{11}), 125.6 (C_{12}), 126.2 (C_{16}), 127.0 (C_{20}); [M+H+] with m/z 331.2757, CHN: Calc. C, 76.7; H, 4.4; N, 7.45; Found: C, 76.2; H, 4.2; N, 7.4.

4,7-dihydroxy-2*H*-chromen-2-one (3)



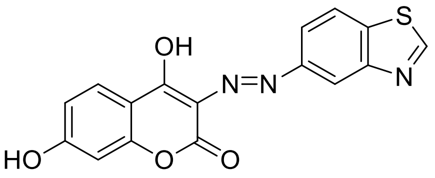
Pale Yellow (Powder), $C_9H_5O_{3,}$ 275-280°C, IR (KBr, cm^{-1}): 1646 (C-H), 1669 (C=C), 3345 (O-H), 1260 (C-O), 1552 (C=O); ^{1}H NMR ($CDCl_3$) δ 3.9 (s, OH), 5.5 (s, 1H), 5.8 (d, 1H), 7.7 (d, 1H), 17.1 (s, OH); ^{13}C NMR ($CDCl_3$) δ 155.1 (C_7), 152.3 (C_9), 158.5 (C_2), 153.5 (C_4), 123.3 (C_5), 112.7 (C_6), 108.7 (C_8), 91.1 (C_3) (m); [M+H+] with m/z 179.1257, 178.0341; CHN: Calc. C, 60.68; H, 3.39, Found C, 60.45; H, 3.26.

4,7-dihydroxy-3-(thiazol-5-yldiazenyl)-2*H*-chromen (4a)



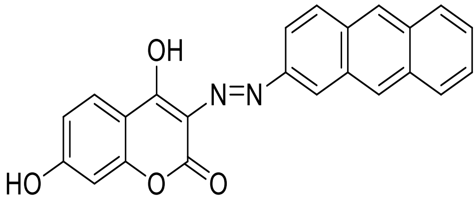
Mustard Yellow (Powder), $C_{12}H_9N_3O_3S$, 180-190°C, IR (KBr, cm^{-1}): 1676 (C-H), 1689 (C=C), 3345 (O-H), 1570 (C=O), 2164 (N=N), 2560 (S-H), 3310 (C-N), 1270 (C-O); ^1H NMR ($CDCl_3$) δ 3.52 (s, OH), 5.27 (s, 1H), 5.57 (d, 1H), 7.39 (dd, 2H), 8.35 (d, 1H), 9.35 (s, 1H), 15.7 (s, OH); ^{13}C NMR ($CDCl_3$) δ 153.8 (C_7), 158.8 (C_4), 155.3 (C_2), 153.7 (C_{11}), 154.6 (C_9), 130.5 (C_5), 130.9 (C_6), 112.5 (C_{10}), 117.2 (C_{12}), 110.1 (C_8)(m), 79.9 (C_3)(m); [M+H+] with m/z 289.0417, 180.1452; CHN: Calc. C, 49.83; H, 2.44; N, 14.53; S, 11.08, Found C, 48.72; H, 2.51; N, 14.9; S, 12.05.

3-(benzothiazol-5-yldiazenyl)-3,7-dihydroxy-2*H*-chromen-2-one (4b)



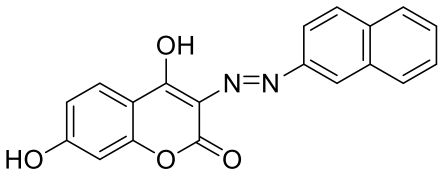
Light Voilet (Powder), $C_{15}H_9N_3O_3S$, 265-285°C, IR (KBr, cm^{-1}): 1610 (C-H), 1690 (C=C), 3350 (O-H), 1670 (C=O), 2145 (N=N), 2500 (S-H), 3230 (C-N), 1290 (C-O); ^1H NMR ($CDCl_3$) δ 5.52 (s, OH), 5.23 (s, 1H), 5.5(d, 1H), 7.2 (dd, 2H), 7.59 (d, 1H), 8.23 (d, 1H), 8.58 (d, 1H), 9.52 (s, 1H), 17.5 (s, OH); ^{13}C NMR ($CDCl_3$) δ 155.9 (C_{11}), 153.8 (C_2), 158.2 (C_4), 155.3 (C_9), 153.5 (C_7), 138.5 (C_{12}), 130.2 (C_5), 101.9 (C_8), 110.0 (C_{10}), 130.7 (C_{12}), 125.1 (C_{15}), 123.5 (C_{14}), 121.8 (C_{13}), 112.7 (C_6), 80 (C_3); [M+H+] with m/z 339.3257, 333.09; CHN: C, 56.63; H, 2.67; N, 12.38; S, 9.45, Found C, 56.41; H, 2.72; N, 12.45; S, 9.54.

3-(anthracene-2-yldiazenyl)-4,7-dihydroxy-2*H*-chromen-2-one (4c)



Green (Powder), $C_{23}H_{13}H_2O_3$, 300-320°C, IR (KBr, cm^{-1}): 1630 (C-H), 1670 (C=C), 3345 (O-H), 1650 (C=O), 2142 (N=N), 1285 (C-O); ^1H NMR ($CDCl_3$) δ 5.3 (s, OH), 5.52 (s, 1H), 5.75 (d, 1H), 7.3 (d, 3H), 7.57 (d, 1H), 7.9 (dd, 3H), 8.3 (d, 1H), 15.7 (s, OH); ^{13}C NMR ($CDCl_3$) δ 153.8 (C_9), 158.3 (C_4), 125.6 (C_{18}), 155.7 (C_7), 125.6 (C_{19}), 153.2 (C_2), 131.7 (C_{14}), 130.2 (C_5), 129.2 (C_{16}), 128.1 (C_{13}), 125.5 (C_{11}), 125.6 (C_{20}), 131.7 (C_{21}), 126.5 (C_{22}), 131.7 (C_{23}), 125.0 (C_{15}), 125.3 (C_{12}), 112.3 (C_6), 110.1 (C_{10}), 101.2 (C_8), 78 (C_3) (m), 128.1 (C_{17}); [M+H+] with m/z 382.0187, 383.1025; CHN: Calc. C, 72.25; H, 3.69; N, 7.33; Found C, 73.12; H, 3.78; N, 7.43.

4,7-dihydroxy-3-(napthalen-1-yldiazenyl)-2*H*-chromen-2-one (4d)



Grey (Powder), $C_{19}H_{12}H_2O_3$, 290-300°C, IR (KBr, cm^{-1}): 1610 (C-H), 1570 (C=C), 3210 (O-H), 1590 (C=O), 2150 (N=N), 1290 (C-O); ^1H NMR ($CDCl_3$) δ 5.35 (s, OH), 5.52 (s, 1H), 5.75 (d, 1H), 7.3 (dd, 3H), 7.59(s, 1H), 8.0 (dd, 3H), 15.7 (s, OH); ^{13}C NMR ($CDCl_3$) δ 153.8 (C_7), 158.1 (C_4), 155.2 (C_2), 153.3 (C_9), 133.8 (C_{14}), 126.2 (C_{17}), 130.5 (C_5), 128.3 (C_{15}), 127.1 (C_{13}), 125.2 (C_{11}), 125.5 (C_{12}), 112.5 (C_6), 110.0 (C_8), 110.5 (C_{10}), 128.2 (C_{18}), 132.8 (C_{19}), 126.2 (C_{16}), 79 (C_3) (m); [M+H+] with m/z 332.0864, 334.0548; CHN: Calc. C, 68.67; H, 3.64; N, 8.43; Found C, 68.54; H, 3.85; N, 8.56.

3. Results & Discussion

3.1 Coloring properties of 3-(thiazole/ benzothiazole/ naphthalene/ anthracene)-7-hydroxy-4-methyl-2*H*-chromen-2-one

3.1.1 Preparation of Dye Dispersion: The required amount of dye (3% shade) was dissolved in 1 mL of acetone and then added dropwise, while stirring, to a solution of an anionic dispersing agent (a polycondensation product of aromatic sulfonic acid and anionic salt). After the solvent evaporated, the dye formed a fine dispersion, making it ready for use in dyeing [7].

3.1.2 Pretreatment of Fabric for Dyeing Process: The desizing process was initially performed to remove pulp and other biological impurities from the fabric. This was followed by scouring, which eliminated a significant portion of inherent contaminants, including lipids, cottonseeds, husk, pectin, and other materials [10,11]. Sodium hydroxide

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was used in the scouring process, after which the fabric was bleached to remove any color and achieve the desired level of whiteness [12,13].

3.1.3 Dyeing of Wool/Cotton/Polyester Fabrics: A dye bath with a dye-to-liquor ratio of 2:30 was prepared in sealed stainless steel dye pots, each with a capacity of 250 ml. An additional dispersing agent, alkyl polyethylene glycol (1.5-3.0 g/L), was added, and the pH of the solution was adjusted to 5.5 using glacial acetic acid. The dyeing procedure involved gradually raising the dye bath temperature from 30 °C to 130 °C at a rate of 3 °C per minute. The temperature was then held at 130 °C for 50 minutes before cooling rapidly to 50 °C at a rate of 9.9 °C per minute. Afterward, the dyed textiles were washed with cold water, treated with sodium hydroxide (2 g/L) and sodium hydrosulfite (2 g/L) to remove impurities, and soaked in a solution of 3% non-ionic detergent and ammonia (pH 8.5) at 50 °C for 30 minutes to improve their wash resistance. **Figures 4-9** illustrate the colors achieved with dyes **(1, 2a-d)** on different fabrics. The properties of the dyed fabrics were evaluated using the grayscale method, which compares the fabric's baseline color to five pairs of gray standards, each representing a different level of color fading. The rating scale ranges from 1 to 5, where 5 indicates no color loss, 1-2 shows high susceptibility to fading, and 3 represents moderate fading [14].

1 **2a** **2b** **2c** **2d**

(Ivory) **(Light Pumpkin)** **(Paris Blue)** **(Ultra Black)** **(Silver Reflective)**

Figure 4 Dyed Polyester Fabrics

1 **2a** **2b** **2c** **2d**

(Sterling) **(Graphite Grey)** **(Cream)** **(Pebble Tan)** **(Bronze)**

Figure 5 Dyed Cotton Fabric

1

2a

2b **2c** **2d**

(Maize) **(Spiced Cider)** **(Ultra Black)** **(Light Coral)** **(Kiwi)**

Figure 6 Dyed Wool Fabrics

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3 **Butter**
4a **Apricot**
4b **Butterfly Blue**
4c **Forest Green**
4d **Stale Grey**

Figure 7 Dyed Polyester Fabrics

3 **Apricot**
4a **Terra Cotta**
4b **Lavender**
4c **Kelley Green**
4d **Pewter**

Figure 8 Dyed Cotton Fabrics

3 **Sunflower**
4a **Mustard**
4b **Light Purple**
4c **Polo Green**
4d **Matte Black**

Figure 9 Dyed Wool Fabric

Upon dyeing, compounds **(1, 2a-d)** exhibited distinct colors on various fabrics. On polyester fabric, the colors ranged from ivory, light pumpkin, Paris blue, ultra black, to silver. On cotton fabric, the colors displayed were sterling, graphite grey, cream, tan, and bronze. On wool, the colors observed were maize, spiced cider, ultra black, light coral, and kiwi. Compounds **(3, 4a-d)** were applied to various fabrics, including polyester, cotton, and wool, yielding an array of colors. Polyester fabric displayed colors ranging from butter, apricot, blue, and green to stale grey. Cotton fabric showed colors from apricot, terra cotta, lavender, and green to pewter. Wool fabric exhibited colors from sunflower, mustard, light purple, and green to black.

3.1.4 Fastness to Washing

Colorfastness to washing refers to a textile's ability to maintain its color when exposed to mechanical agitation in a soap solution, followed by rinsing and drying. During this process, the textile is in contact with one or two specified adjacent fabrics under controlled time and temperature conditions. The change in the color of the sample and the fading of the neighboring fabric are assessed using grey scales. The high level of fastness may be attributed to the limited dispersion of dye molecules within the textile material **(Table 1, Figure 10),** [7].

3.1.5 Fastness to Perspiration (Acid and Alkaline)

The fastness to perspiration test method is used to evaluate a material's ability to retain its color when exposed to human sweat over an extended period. The stability of the dyes **(1, 2a-d)** is attributed to their resistance to degradation in both acidic and basic environments **(Table 1, Figure 11)** [7].

Table 1 Washing Fastness & Perspiration Properties of 3-(thiazole/ benzothiazole/ naphthalene/ anthracene)-7-hydroxy-4-substituted-2*H*-chromen-2-one

Washing				**Perspiration**					
				Acidic			**Alkali**		
Dye no.	**Cotton**	**Wool**	**Polyester**	**Cotton**	**Wool**	**Polyester**	**Cotton**	**Wool**	**Polyester**
1	4	3	3	3	3	3	3	5	3
2a	3	3	3	4	3	3	5	3	3
2b	4	4	3	3	3	5	5	3	4
2c	3	3	4	3	3	3	5	3	3
2d	2	3	3	3	4	5	3	2	3
3	2	2	3	3	2	3	3	3	3
4a	3	4	3	3	3	4	3	4	3
4b	3	3	4	3	2	3	3	3	4
4c	3	2	5	4	2	5	4	3	3
4d	3	2	3	3	3	3	3	2	3
Methyl Orange	3	3	3	3	3	3	3	3	3

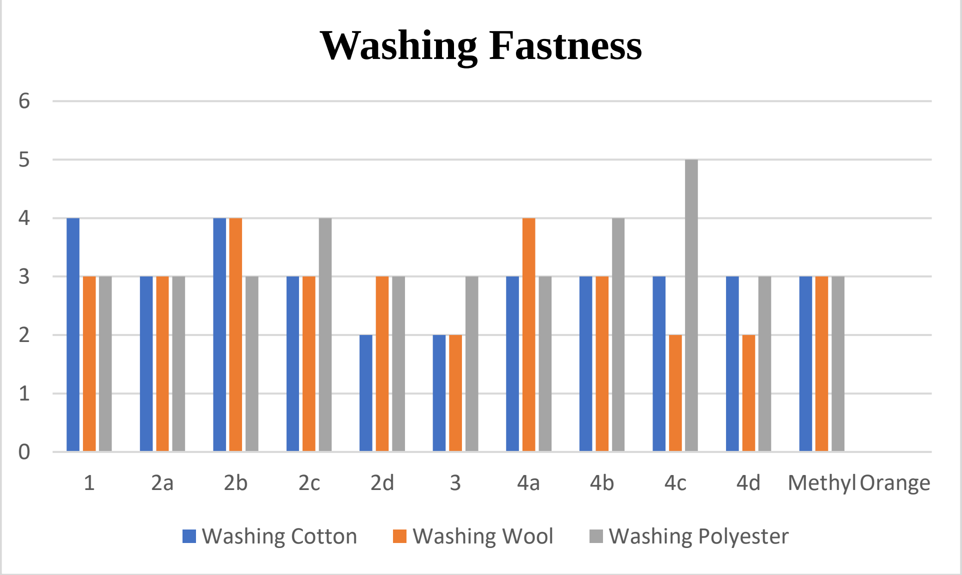


Figure 10 Washing Fastness of Dyeing Fabrics

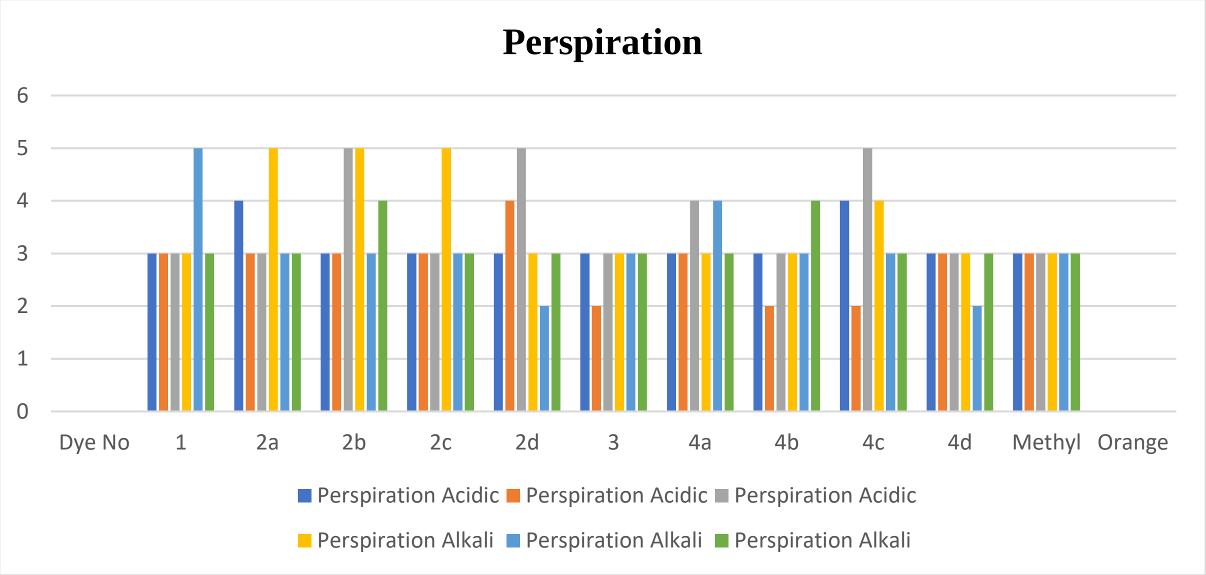


Figure 11 Perspiration of Synthesized Dyes in an Acidic & Alkali Medium

3.1.6 Dyeing and Fastness Determination

The fastness properties of the dyed fabrics are presented in **Tables 2-4** and **Figures 12-14**. In the majority of the dyed fabric samples, the performance falls within the range of 2-5. For light fastness, all the dyed fabrics exhibit good to excellent results on polyester fabric. Additionally, samples dyed with anthracene demonstrate superior rubbing and washing fastness on polyester fabric [7].

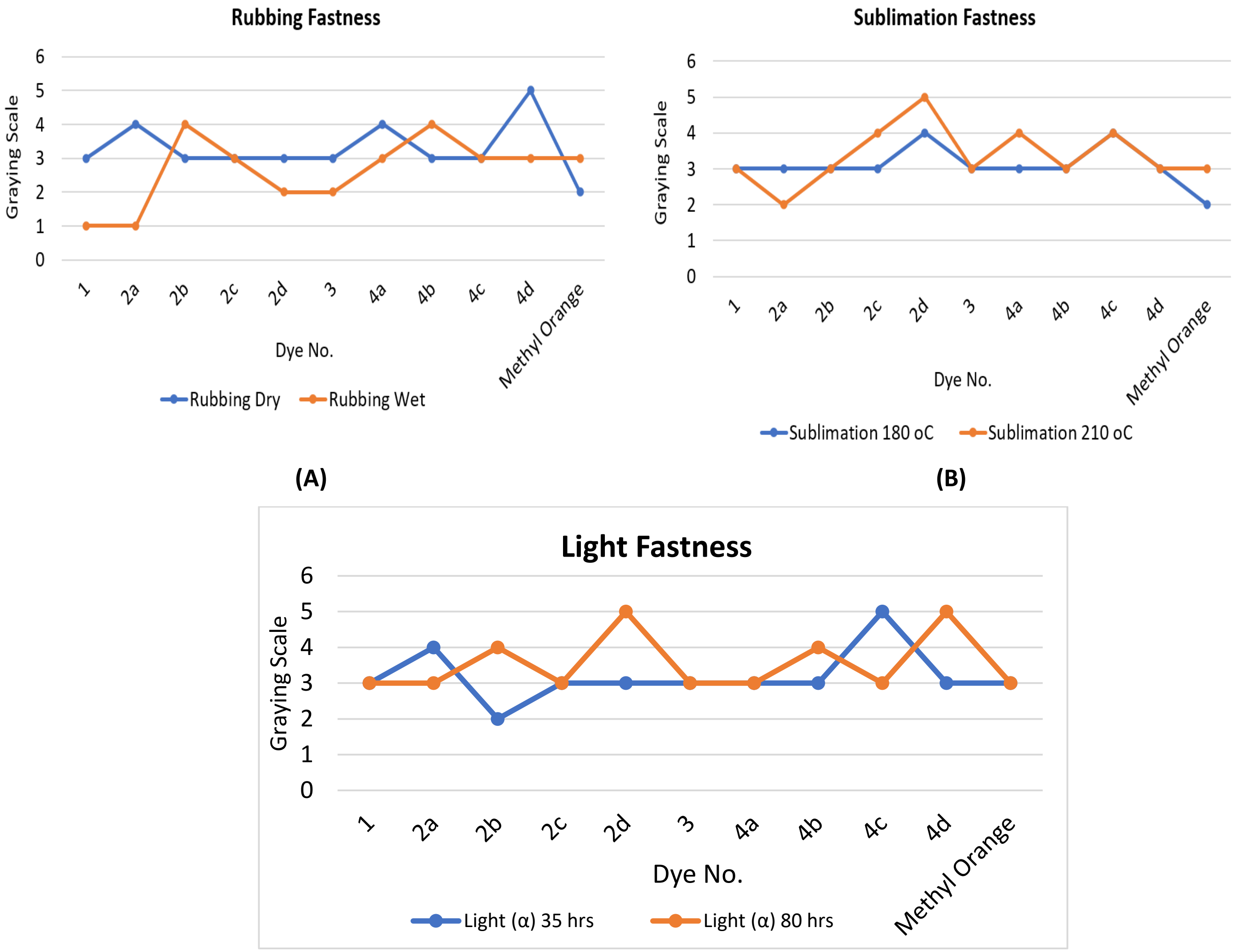
3.1.7 Colorfastness Tests

The HTHP (high temperature and high pressure) method at 130 °C treated fabrics with synthetic dispersion dye at a 3% shade. The fastness properties of the synthesized dyes applied to the materials were then assessed [7].

Table 2 Fastness Properties of synthesized 3-(thiazole/ benzothiazole/ naphthalene/ anthracene)-7-hydroxy-4-substituted-2*H*-chromen-2-one Dyes on Polyester Fabric

Dye No.	**Rubbing**		**Sublimation**		**Light (α)**	
	Dry	**Wet**	**180 °C**	**210 °C**	**35 hrs**	**80 hrs**
1	3	1	3	3	3	3
2a	4	1	3	2	4	3
2b	3	4	3	3	2	4
2c	3	4	2	3	3	3
2d	3	5	4	3	3	5
3	3	2	3	3	3	3
4a	4	3	3	4	3	3
4b	3	4	3	3	3	4
4c	3	3	4	4	5	3
4d	5	3	3	3	3	5
Methyl Orange	2	3	2	3	3	3

α = Light Fastness, 1-5 Scale, Rubbing, Sublimation Fastness, 1-5 Scale



(A) (B)

(C)

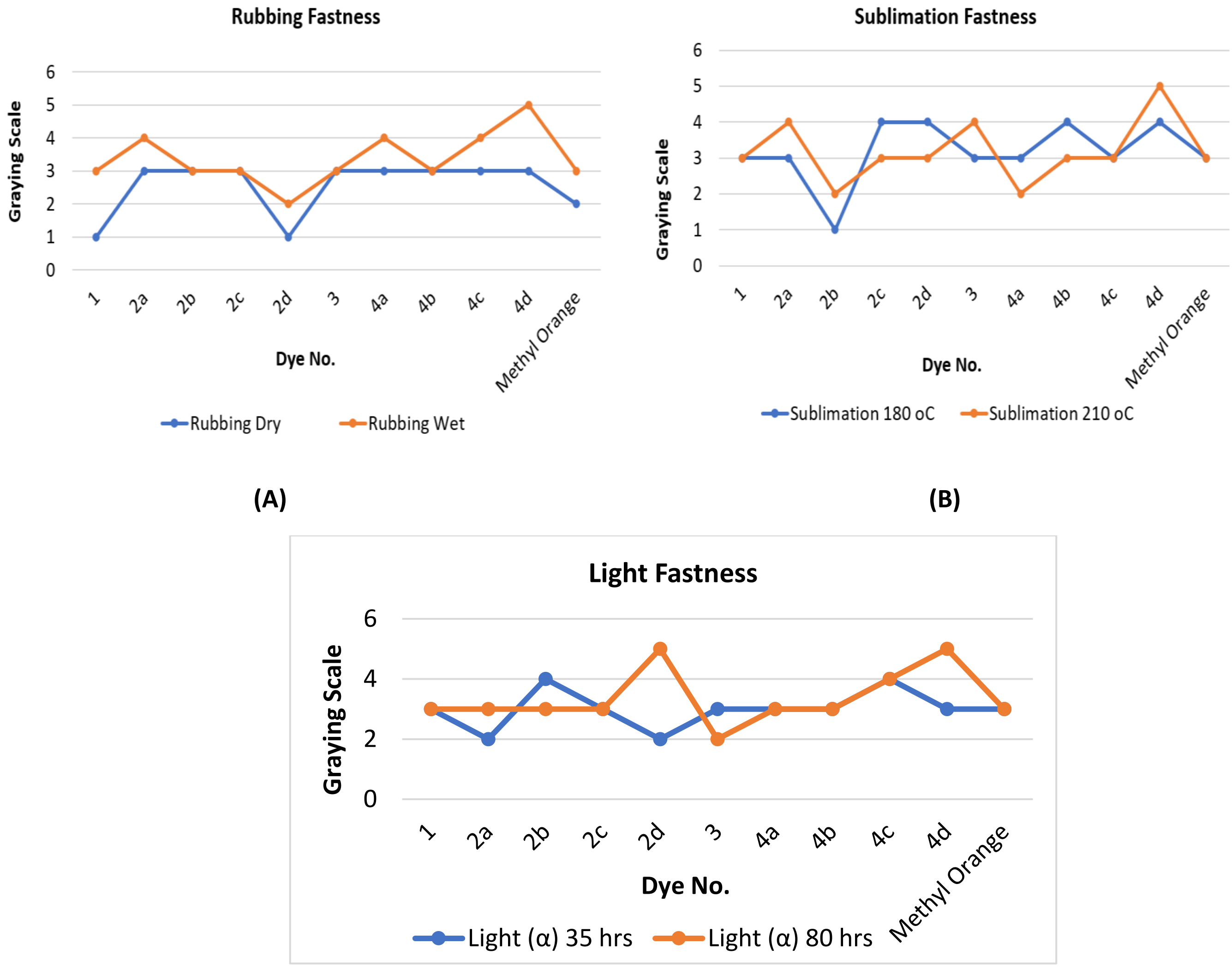
Figure 12 (A) Rubbing Fastness Property Under Dry and Wet Conditions, (B) Sublimation Fastness at 180 °C and 210 °C, and (C) Light Fastness at 35 hrs and 80 hrs on Polyester Fabric

Table 3 Fastness Properties of Synthesized 3-(thiazole/ benzothiazole/ naphthalene/ anthracene)-7-hydroxy-4-substituted-2*H*-chromen-2-one Dyes on Cotton Fabric

Dye No.	Rubbing		Sublimation		Light (α)	
	Dry	Wet	180 °C	210 °C	35 hrs	80 hrs
1	1	3	3	3	3	3
2a	3	4	3	4	2	3
2b	3	3	1	2	4	3
2c	3	3	4	3	3	3
2d	1	2	4	3	2	5
3	3	3	3	4	3	2
4a	3	4	3	2	3	3

4b	3	3	4	3	3	3
4c	3	4	3	3	4	4
4d	3	5	4	5	3	5
Methyl Orange	2	3	3	3	3	3

α = Light Fastness, 1-5 Scale, Rubbing, Sublimation Fastness, 1-5 Scale



(A) **(B)**

(C)

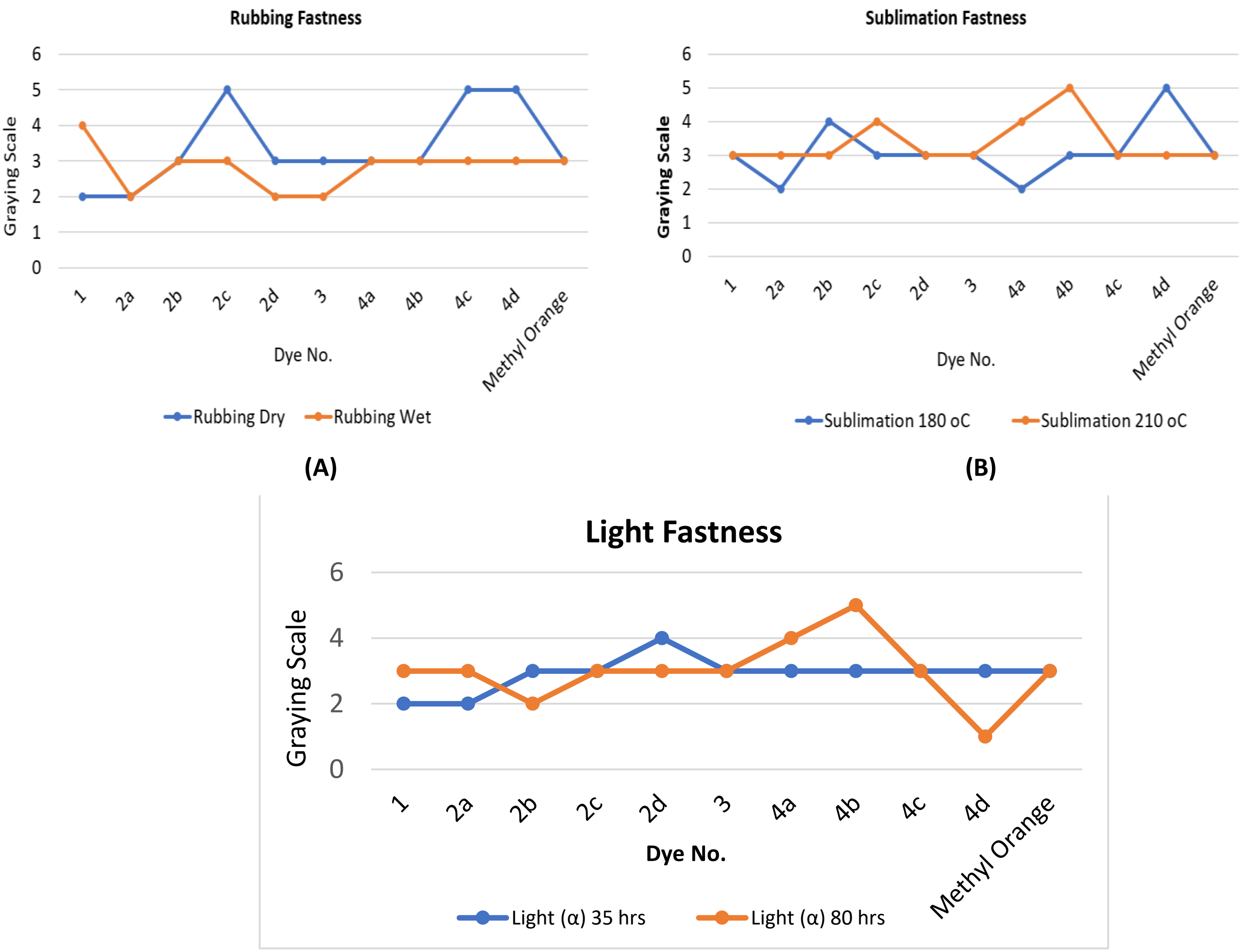
Figure 13 (A) Rubbing Fastness Property Under Dry and Wet Conditions, (B) Sublimation Fastness at 180 °C and 210 °C, and (C) Light Fastness at 35 hrs and 80 hrs on Cotton Fabric

Table 4 Fastness Properties of Synthesized 3-(thiazole/ benzothiazole/ naphthalene/ anthracene)-7-hydroxy-4-substituted-2*H*-chromen-2-one Dyes on Wool Fabric

Dye No.	**Rubbing**		**Sublimation**		**Light (α)**	
	Dry	**Wet**	**180 °C**	**210 °C**	**35 hrs**	**80 hrs**
1	2	4	3	3	2	3
2a	2	2	2	3	2	3
2b	3	3	4	3	3	2

2c	5	3	3	4	3	3
2d	3	2	3	3	4	3
3	3	2	3	3	3	3
4a	3	3	2	4	3	4
4b	3	3	3	5	3	5
4c	5	3	3	3	3	3
4d	5	3	5	3	3	1
Methyl Orange	3	3	3	3	3	3

α = Light Fastness, 1-5 Scale, Rubbing, Sublimation Fastness, 1-5 Scale



(A)

(B)

(C)

Figure 14 (A) Rubbing Fastness Property under Dry and Wet Conditions, (B) Sublimation Fastness at 180 °C and 210 °C, and (C) Light Fastness at 35 hrs and 80 hrs on Wool Fabric

3.1.8 Color Assessment

The K/S value, used to represent dye uptake or color strength, was determined for each dyed specimen as well as the undyed sample at the maximum absorption wavelength of 370 nm. This was calculated from the reflectance values using the Kubelka-Munk equation [15] $\boldsymbol{K/S} = (\mathbf{1}-\boldsymbol{R})^2 / \mathbf{2}\boldsymbol{R}$. Here, K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance value of the fabric at the maximum wavelength. The original dyestuff of each group is used as the standard for calculating the color difference. The results obtained using CIE techniques are shown in **Table 5** and **Figure 15.**

Table 5 Color Value of Synthesized Dyes on Different Fabrics

Fabric	Dye no.	L	A	B	K/S at 370 nm
Cotton	**1**	80.253	3.052	3.075	0.757
	2a	77.822	5.253	3.271	0.922
	2b	72.33	3.251	3.307	1.5
	2c	70.723	3.121	3.279	2.55
	2d	73.35	5.23	2.33	0.95
	3	55.23	3.3522	3.125	0.897
	4a	59.55	3.589	3.985	1.212
	4b	70.250	5.255	5.255	1.355
	4c	75.523	7.2135	5.780	2.891
	4d	81.298	9.235	8.235	5.213
	Methyl Orange	55.23	3.12	3.235	1.25
Wool	**1**	51.727	0.358	5.353	1.315
	2a	38.527	-0.011	10.201	3.282
	2b	55.252	1.012	9.21	3.23
	2c	81.835	1.95	-1.133	0.595
	2d	72.55	2.01	5.57	0.85
	3	52.23	1.255	3.23	1.351
	4a	50.559	1.891	5.233	2.323
	4b	72.155	3.255	7.251	3.152
	4c	80.125	5.255	5.235	3.895
	4d	81.232	8.255	10.235	3.551
	Methyl orange	85.23	3.57	3.13	2.01
Polyester	**1**	81.107	2.803	3.317	1.007
	2a	73.005	5.393	3.831	1.023
	2b	73.732	3.053	3.0837	3.55
	2c	57.82	2.32	3.55	2.01
	2d	83.23	5.23	3.25	1.55
	3	71.250	3.02	2.55	1.595
	4a	73.235	3.235	3.235	2.027
	4b	55.231	5.893	5.231	2.255
	4c	82.78	5.215	7.589	5.55
	4d	91.258	10.235	12.553	3.558

	Methyl orange	93.25	3.21	3.23	2.25

*Where, K/S = Color Strength, K = absorption coefficient, S = Scattering coefficients, L = Lightness/Darkness, a = Redness/Greenness, b = Yellowness/Blueness

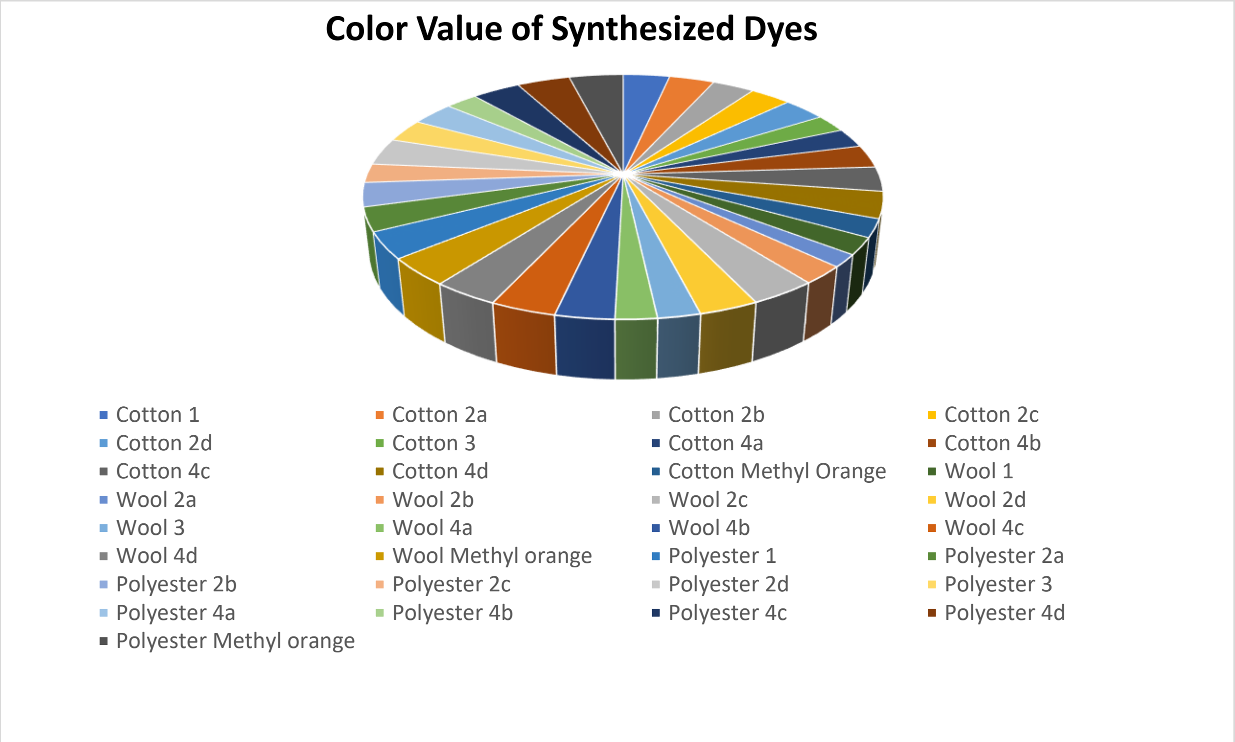


Figure 15 Color Value of Dyes on Different Fabric

All of the compounds **(1, 3, 2a-d, 4a-d)** exhibited Ar-OH peaks at approximately 3512-3577 cm^{-1} and C=O at approximately 1700-1733 cm^{-1}. The presence of –C-N str. in all compounds was indicated by the peak range 1521-1593 cm^{-1}. The IR spectra of all the compounds examined exhibit a peak in 1521-1593 cm^{-1} range, which implies that they all contain a carbon-nitrogen double bond (–C=N–). IR radiation in this wavenumber range is typically absorbed by this bond as a result of its characteristic stretching vibrations. The presence of –C-H stretching vibrations as a result of methyl substitution was indicated by the infrared (IR) spectrum, which exhibited maxima in the 2823-2992 cm^{-1} interval. Furthermore, the presence of aromatic –C-H and –C=C stretching vibrations was indicated by peaks in the 1380-1550 cm^{-1} range. The melting points of all synthesized compounds were determined to confirm the structures of the newly synthesized compounds, and both ^{1}H and ^{13}C NMR analyses were conducted. In this study, substitution reactions were executed at the 7th and 4th positions of the coumarin ring using various primary and secondary amines and hydroxy groups, with the success of these substitutions confirmed through spectral data. This synthesis process resulted in the production of 7-hydroxy-4-methyl coumarin **(1)**, and 4,7-dihydroxy coumarin **(3)**, along with their derivatives **(2a-d, 4a-d)**, utilizing heterocyclic compounds such as thiazole, benzothiazole, naphthalene, and anthracene. All 10 synthesized compounds were tested on three fabrics: polyester, cotton, and wool. The dyeing characteristics of all synthesized compounds, such as light fastness, washing fastness, sublimation fastness, and color positions in CIE coordinates, were assessed to evaluate the dyeing properties of all synthesized compounds. Compound **1** exhibited excellent sublimation fastness at 180°C, while compound **2b** demonstrated sublimation fastness at 210°C on polyester fabric. Compounds **1**, **2a**, **2b**, **2c**, and **2d** showed good light fastness over 35 hours, with compounds **2c** and **2d** showing even better performance over 80 hours. The color values for compounds **(1, 2a-d)** on the polyester fabric were 1.00, 1.02, 3.55, 2.01, and 1.55, respectively. Dye **2b** exhibited a higher K/S value due to the presence of a heterocyclic group. Dyes **3**, **4a**, **4b**, **4c**, and **4d** displayed improved light fastness at 80 hours. The color values for compounds **(3, 4a-d)** on the polyester fabric were 1.59, 2.02, 2.25, 5.55, and 3.55, respectively. Similar tests were performed on cotton, polyester, and wool fabrics, with the best performance observed on polyester fabric.

4. Conclusions

The objective of this paper was to synthesize and characterize a series of 7-hydroxy-4-substituted coumarins. The synthesized compounds **(1, 3, 2a-d, 4a-d)** were evaluated for their dyeing properties, including washing fastness, sublimation fastness, light fastness, and color values on various fabrics, including polyester, cotton, and wool. Compound **1** exhibited excellent sublimation fastness at 180°C, whereas compound **2b** demonstrated sublimation fastness at 210°C on polyester fabric. Compounds **1, 2a, 2b, 2c,** and **2d** all showed good light fastness for more than 35 hours, with compounds **2c** and **2d** performing even better, lasting up to 80 hours. The color values for compounds **(1, 2a-d)** on the polyester fabric were 1.00, 1.02, 3.55, 2.01, and 1.55, respectively. Dye **2b** exhibited a higher K/S value due to the presence of a heterocyclic group. Dyes **3, 4a, 4b, 4c,** and **4d** displayed improved light fastness over 80 hours. The color values for compounds **(3, 4a-d)** on the polyester fabric were 1.59, 2.02, 2.25, 5.55, and 3.55, respectively. It was concluded from the observed data that the synthesized dyes show better dyeing properties on polyester fabric.

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Competing interests

The authors declare that they have no competing interests.

Availability of data and materials

Provided in Manuscript.

Ethics approval and consent to participate

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