



## SYNTHESIS OF SOME NEW AZO DYES ON THE BASE OF 6-AMINOCOUMARINE

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### Abstract:

Diazotization and azo coupling reactions are versatile tools of fine organic synthesis. Azo dyes have very interesting physical, spectral and chemical properties and are widely used in the different fields of the science and technology. Moreover, some of them have very significant biological activity and are used in the healthcare or medical diagnostics. Coumarin belongs to chromene type dyes, but it may be used as an azo partner in the azo coupling reaction for the synthesis of azochromenes dyes.

In the current research we have obtained four new dyes bearing two  $\pi$ -conjugated azo and chromene chromophores. The target compounds were synthesized by diazotization of 6-aminocoumarin (**1**) and with following azo coupling to 2-hydroxybenzoic acid (**3a**), naphthalen-2-ol (**3b**), 4-amino-5-hydroxynaphthalene-2,7-disulfonic acid (**3c**) and (E)-3-(4-hydroxyphenyl)acrylic acid (**3d**). Obtained azo dyes have been used for dyeing wool fiber and various technical and spectral properties have been studied.

**Keywords:** azo dyes, diazotization, azo coupling, dyeing, wool

### Introduction

Diazotization and azo coupling reactions are versatile tools of fine organic synthesis. These consecutive reactions commonly are used for the generation of azo chromophore and colored materials, having ability to color other substances. Azo dyes have very interesting physical, spectral and chemical properties and are widely used in the different fields of the science and technology. Moreover, some of them have very significant biological activity and are used in the healthcare or medical diagnostics. Azo dyes usually are in close contact to human body and potentially may penetrate into organism in some quantity and undergo metabolism process forming mutagenic and toxic primary aromatic amines. Therefore, it is very important to choose the non-toxic, eco- or biofriendly diazo and azo partners during azo compound construction. On the other hand, the conjunction strategy of different chromophores into one molecule structure for the aim of physical, chemical and biological properties synergizes, is another modern technique in the design of the dyes.

Coumarin belongs to chromene type dyes, but it may be used as an azo partner in the azo coupling reaction for the synthesis of azochromenes dyes [1, 2]. While 6-aminocoumarin easily reacts to sodium nitrite in the presence of hydrochloric acid and gives corresponding diazonium salt, able to couple aromatic substances and form azo compounds. A series of sulfocoumarin-, coumarin-, and 4-sulfamoylphenyl-bearing indazole-3-carboxamide hybrids with the selective inhibition properties of tumor-associated carbonic anhydrase isozymes IX and XII have been

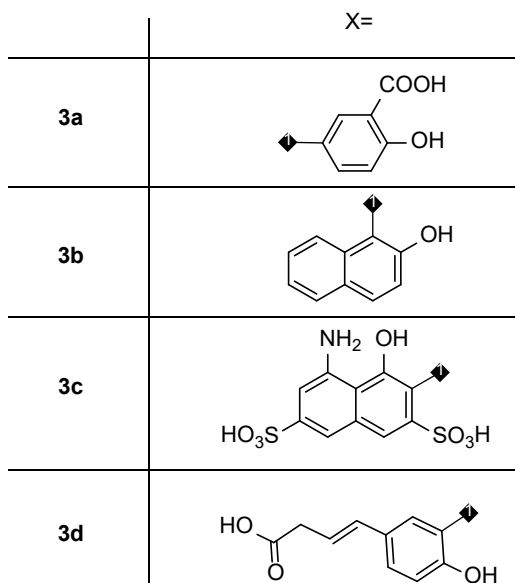
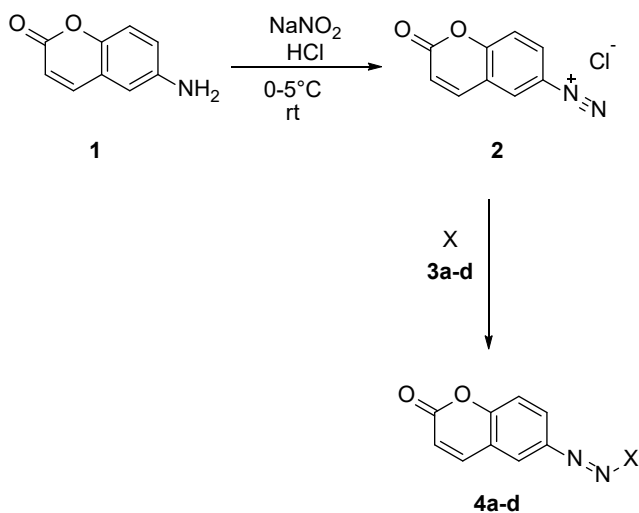
synthesized by S. Angapelly and co-workers [3]. Moreover, coumarin azo derivatives which may be used as a dyes [4], fluorescent probes [5], antimicrobial [6-9], gelling [10], antithrombotic [11] agents, Xa inhibitors [12], etc [13].

### Results and Discussion

In the current research we have obtained four new dyes bearing two  $\pi$ -conjugated azo and chromene chromophores. The target compounds were synthesized in accordance with two sequential stages of diazotization-azo coupling, as shown on scheme 1. 6-aminocoumarin (**1**) was chosen as the diazo partner, and 2-hydroxybenzoic acid (**3a**), naphthalen-2-ol (**3b**), 4-amino-5-hydroxynaphthalene-2,7-disulfonic acid (**3c**) and (E)-3-(4-hydroxyphenyl) acrylic acid (**3d**) for azo partners.

Diazotization of **1** has been carried out in the diluted hydrochloric acid media by the action of sodium nitrite at 0-5 °C under stirring for a period of 60 min. The finishing of the process was checked by the positive test on starch-iodine paper (generation of blue color indicates the excess of nitrous acid). The excess of nitrous acid has been removed by the addition of solid urea until terminating gas evaluation from the reaction mass. Finally, diazonium salt in the form of water solution was filtered off quickly on the filter paper in the ice bath for avoiding decomposing of **2**. Purified solution of **2** has been used immediately in the azo coupling reaction with preliminarily prepared and cooled to 0°C alkali solutions of azo partners **3a-d**.

The azo coupling reactions were carried out by adding diazotization partner solution to the azo partner solution under vigorous stirring and careful monitoring of pH value. To convert phenolic and naphthol compounds into more reactive forms of phenolates and naphtholates, it is imperative to maintain a slightly alkaline pH value of about 9-10. Thus, a constant pH was adjusted from time to time by adding a 10% NaOH solution throughout the azo coupling process. The final compounds have been precipitated by adding 10% hydrochloric acid solution to pH value of 7 and isolated by filtration. The solid remains have been washed out

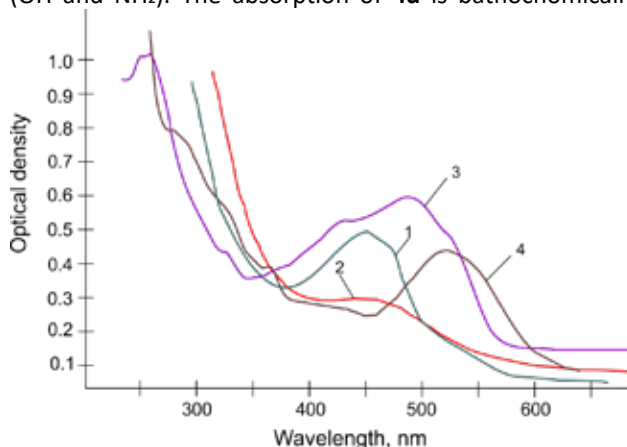


**scheme 1. Synthesis of azo-coumarin dyes by diazotization-azo coupling reactions**

by cold water on the filter paper, transferred to Petri dish and dried at ambient temperature in the vacuum.

The isolated azo dyes have been used for dyeing without additional purifications except of **4d**, which was recrystallized in 1% HCl solution. The yields of final products were 40-55% (table 1, fig. 1.).

Analysis of the UV-vis spectra shows, that all obtained dyes have absorption in the visible range. **4c** absorbs on the 520 nm wavelength because of longest  $\pi$ -conjugated system and bearing two strength electron donating groups (OH and  $\text{NH}_2$ ). The absorption of **4d** is bathochromically



**Fig. 1. UV-vis spectra: 1 – 4a, 2- 4b, 3-4c, 4- 4d**

shifted in comparison of 4a absorption value which caused by participation of exocyclic double bond in the  $\pi$ -conjugated system.

Coumarin-Azo dyes have been used for dyeing of wool fiber iCoumarin-Azo dyes have been used for dyeing of wool fiber in accordance with the method described by M. Toussiro et al [14]. The preliminarily washed up, dyed and weight up fiber was put and soaked in pre-dyeing bath, containing potassium aluminum sulfate (0.3% weight of fiber). The temperature of the bath was increased up to 60°C and kept for 45 min. Then the dyeing bath was cooled to room temperature. Mordanted fiber was washed out with tap water to remove the excess of potassium aluminum sulfate.

For the dyeing bath, a M:L (material to liquor ratio) at 1:40 was used. The mordanted wrung out fiber was put in the dyeing bath and heated again up to 60 °C for a period of 45

**Table 1. The yields and properties of 4a-d**

N	Dye	Yield, %	$\lambda_{\text{max}}(\epsilon)$ , nm, solvent	Dye uptake, %	Lab-coordinates
1	<b>4a</b>	55	440 ( $1.50 \times 10^5$ ), water	80	L=78, b=1, b=62
2	<b>4b</b>	53	480 ( $1.486 \times 10^5$ ), ethanol	60	L=50, b=31, b=56
3	<b>4c</b>	54	520 ( $1.9412 \times 10^5$ ), water	75	L=11, b=27, b=2
4	<b>4d</b>	40	460 ( $1.7647 \times 10^5$ ) water	74	L=78, b=1, b=70

min with manual periodical stirring. The fiber in bath were allowed to cool down, and then rinsed with tap water and left for drying at room temperature.

Dye uptake properties of all dyes **4a-d** have been determined. For this aim, the absorbance of the dyeing bath has been measured before and after dyeing. The dyebath was cooled to room temperature prior to measures. The percentage of dye exhaustion (DE) was calculated according to the given formula:

$$DE = [(A_0 - A_1)/A_0] \times 100$$

where  $A_0$  and  $A_1$  are absorbances of the dye bath, before and after dyeing respectively.

The color strength and color depth of the dyed samples were determined in CIELab coordinates.  $L^*$  corresponds to the brightness (100 % white, 0 – black,  $a^*$  is red-green balance ( $+a^*$  = red,  $-a^*$  = green) and  $b^*$  is the yellow-blue balance ( $+b^*$  = yellow,  $-b^*$  = blue). For the aim of color coordinate measurement, the high-resolution standardized screen has been used with graphical software. The dyed samples have been positioned on graphical square of the horizontally located screen surface. The color of the graphical square was changing programmatically until achieving corresponding color and the Lab-coordinate values have been recorded (see table 1).

The dyed samples have been studied light fastness and stability against wet treatment. For the light-fastness test 4 cm<sup>2</sup> dyed fiber sample was placed on the white surface, irradiated by UV light for 2 hours and re-measured the color according to above described method. Finally, the fastness has been calculated using the following relationship:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

where  $\Delta L = L^*_{\text{after}} - L^*_{\text{before}}$ ;  $\Delta a = a^*_{\text{after}} - a^*_{\text{before}}$ ;  $\Delta b = b^*_{\text{after}} - b^*_{\text{before}}$

The fastness against wet treatment has been performed and resistance against extraction by Soap, HCl, NaOH and

**Table 2. Light fastness and stability against wet treatment of 4a-d**

N	Dye	Light fastness %	Soap, 5%	HCl, 5%	NaOH, 5%	Organic Solvents (EtOH)
1	<b>4a</b>	90	94	92	86	94
2	<b>4b</b>	85	93	92	88	94
3	<b>4c</b>	80	91	90	81	96
4	<b>4d</b>	93	95	93	87	94

ethanol have been carried out. The color changes have been calculated as described above and the results are listed in the table 2.

### Experimental Section

All of the chemicals used were of commercial grade and were further purified by recrystallization and redistilled before use. The solvents were spectroscopic grade. UV-Vis absorption spectra were measured on spectrophotometer Shimadzu UV-1900 (Japan). Fastness to light, sublimation, respiration and wash fastness were assessed in accordance with valid state standards [15, 16]. The dyeing of wool fiber was carried out and exhaustion of the dyed fibers was determined according to the literature [17].

**2-oxo-2H-chromene-6-diazonium chloride (2).** 1.24 mmol (0.2 g) 6-aminocoumarin (**1**) and 1.46 ml 10% hydrochloric acid was placed in the chemical beaker, equipped with magnetic stirrer and thermometer, and dissolved. After complete dissolving of amine **1**, the reaction mass was cooled up to 0°C by using ice-water bath. 1.3 mmol (0.09 g) NaNO<sub>2</sub> in 2 ml water was added dropwise for a period of 30 min under vigorous stirring and keeping temperature below 5°C. The excess of nitrous acid was checked after 30 min of complete addition of NaNO<sub>2</sub> solution and was removed by addition of solid urea in the case of necessity. Finally, the solution of **2** was filtered quickly and used immediately in the azo coupling reaction.

**Azo coupling reaction (General method).** The solution of **2** was added dropwise to a solution of **3a-d** (1.20 mmol) in minimal amount of sodium hydroxide (10%, 25 mL) over a period of 15 min with constant vigorous stirring. The reaction mixture was further stirred for a period of 1 hour and neutralized with hydrochloric acid (10%). The solids, formed after neutralization, was filtered, washed with water, dried and crystallized from ethanol.

**4a:** Yield 0.66 mmol (0.204 g, 55%).  $\lambda_{\text{max}}(\epsilon)$ , nm, solvent: 440 ( $1.50 \times 10^5$ ), water. Yellow crystals ( $L=78$ ,  $b=1$ ,  $b=62$ ).

**4b:** Yield 0.64 mmol (0.201 g, 53%).  $\lambda_{\text{max}}(\epsilon)$ , nm, solvent: 480 ( $1.486 \times 10^5$ ), ethanol. Dark reddish-brown crystals ( $L=50$ ,  $b=31$ ,  $b=56$ ).

**4c:** Yield 0.65 mmol (0.318 g, 54%).  $\lambda_{\text{max}}(\epsilon)$ , nm, solvent: 520 ( $1.9412 \times 10^5$ ), water. Dark brown crystals ( $L=11$ ,  $b=27$ ,  $b=2$ ).

**4d:** Yield 0.48 mmol (0.168 g, 40%).  $\lambda_{\text{max}}(\epsilon)$ , nm, solvent: 460 ( $1.7647 \times 10^5$ ) water. Dark yellow crystals ( $L=78$ ,  $b=1$ ,  $b=70$ ).

### Conclusion

We are able to suggest that 6-aminocoumarin may be used as a diazo partner in the azo coupling reaction for obtaining dyes, bearing both coumarin and azo chromophores

and characterized good spectral and technical properties.

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## გომიერთი ახალი აზო საღებრის სინთეზი 6-ამინოკუმარინის საფუძველზე

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**რეზიუმე.** დიაზოტირებისა და აზომუდლების რეაქციები ორგანული სინთეზის ერთ-ერთ მნიშვნელოვან მეთოდს წარმოადგენს. აზო საღებრებს გააჩნიათ საინტერესო ფიზიკური, სპექტრული და ქიმიური თვისებები. ისინი ფართოდ გამოიყენებიან მეცნიერებისა და ტექნიკის სხვადასხვა სფეროში. უფრო მეტიც, არაერთ აზოსაღებარს აქვს მდიდარი ბიოლოგიური თვისებები, რის გამოც გამოიყენებიან მედიცინასა და დიაგნოსტიკაში. კუმარინი მიეკუთვნება ქრომენული კლასის საღებრებს, თუმცა შესაძლებელია მისი გამოყენება აზო პარტნიორად აზომუდლების რეაქციებში, რომლის დროსაც მიიღება აზოქრომენული საღებრები.

წინამდებარე კვლევაში მიღებულია ოთხი ახალი საღებარი, რომლებიც მოიცავენ შეუღლებულ ორ ქრომოფორულ -აზო და ქრომენულ ქრომოფორს. მიზნობრივი ნაერთები სინთეზირებულია 6-ამინოკუმარინის (1) დიაზოტირებითა და აზომუდლებით 2-ჰიდროქსიბენზომჟავასთან (3a), 2-ნაფთოლთან (3b), 4-ამინო-5-ჰიდროქსინაფთალინ-2,7-დი-სულფოჟავასთან (3c) და (E)-3-(4-ჰიდროქსიფენილ)აკრილმჟავასთან (3d). მიღებული აზო საღებრები გამოყენებულია შალის ბოჭკოს შესაღებად და შესწავლილია სხვადასხვა ტექნიკური და სპექტრული თვისებები.

**საკვანძო სიტყვები:** აზო საღებრები, დიაზოტირება, აზოდუღლება, ღებვა, შალი