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ICCBIKG 2021

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BOOK OF PROCEEDINGS

October 26-27th, 2021,
Kragujevac, Serbia

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A NOVEL AZO-AZOMETHINE DYE: SYNTHESIS, DYEING AND ANTIOXIDANT PROPERTIES

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Abstract

Schiff bases, or azomethine compounds, are commonly employed in the fields of organic synthesis, metal complexes, materials, and engineering. Especially, they have gained importance in medicinal researches, considering their antimicrobial, anticancer, anti-inflammatory, and antioxidant properties. On the other side, azo dyes are the most significant group of synthetic dyes, utilized in textile fiber dyeing. Conjugation of Schiff bases with azo compounds leads to the class of azo-azomethine dyes, which have numerous applications related to their coloration and biological properties. Viscose is a textile material widely used in the medicine. Moreover, viscose fiber can be engineered in many ways which are significant in the development of medical materials. The antioxidant effect is an important feature of medical textiles, such as wound dressings. In this work, the microwave-assisted synthesis and characterization of novel azo-azomethine dye are reported. The azo-azomethine dye is obtained by the condensation between arylazo pyridone dye and 4-aminophenol. The structure of synthesized dye was determined by ATR-FTIR, NMR, and UV-Vis spectroscopy. Azo-azomethine dye was used for dyeing viscose, and the washing fastness of dyed material was evaluated according to the standard method. The viscose fabrics, before and after washing, were analyzed in terms of their color coordinates in the CIELab color space. The antioxidant properties of azo-azomethine dye and dyed viscose fabrics were examined by the ABTS method.

Keywords: 2-pyridone, viscose, free radical scavenging effect, medicinal textiles

1. Introduction

Azo pyridone dyes are a well-known class of disperse dyes, characterized by good color strength, excellent light fastness properties, bright hues, and luminous colors [1]. Moreover, they possess pharmacological activities, and also are utilized in the dye industry [1,2]. On the other side, there is considerable interest in Schiff base ligands and their complexes due to their numerous biological properties [3]. Therefore, azo-azomethine dyes represent a very interesting class of organic compounds, since they can exhibit biological activities, as well as, be excellent dyestuffs [4]. The viscose fabric is often used for medical purposes due to its high absorbency, breathability, comfort, and softness. Taking that into account, the antioxidant effect is an important feature of medical materials [5].

In this regard, we are reporting the microwave-assisted synthesis of novel azo-azomethine dye, based on arylazo pyridone structure. The structure of synthesized dye was determined by ATR-FTIR, ^{1}H NMR and UV-Vis spectra. Furthermore, viscose fabric has been dyed, and its washing fastness was evaluated. The viscose fabrics, before and after washing, were analyzed in terms of their color coordinates in the CIELab color space. The antioxidant properties of azo-azomethine dye and dyed viscose fabrics were examined by the ABTS method.

2. Experimental part

2.1 Synthesis of 6-hydroxy-4-methyl-2-oxo-5-((4-((hydroxyphenylimino)methyl)phenyl)diazenyl)--1,2-dihydropyridine-3-carbonitrile

The azo dye, 3-cyano-5-(4-formylphenylazo)-6-hydroxy-2-pyridone has been synthesized according to the reported method [6], and afterward, it was used for the preparation of azo-azomethine dye. In the reaction vial, the aforementioned azo dye (**a**) (0.5 mmol, 0.141 g) was dissolved in *N,N*-dimethylformamide (4 mL), and then 4-aminophenol (**b**) (0.5 mmol, 0.055 g) along with 3 drops of acetic acid were added. The reaction mixture was irradiated in the microwave reactor (Anton Paar Monowave 300) for 5 minutes at the temperature of 100 °C. The reaction mixture was cooled down to room temperature and water (10 mL) was added in order to precipitate azo-azomethine dye (**1**). The resulting solid product was collected by filtration and then air dried. The synthesis of azo-azomethine dye is presented in Fig. 1. Dark red powder; yield 75%; m.p. > 300 °C; ATR-FTIR (ν/cm^{-1}): 3137 (NH), 2220 (CN), 1652 (C=O), 1620 (N=C); ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 2.54 (3H, s, CH_3), 6.80 (2H, d, J = 8.4 Hz, Ar-H), 7.21 (2H, d, J = 8.4 Hz, Ar-H), 7.77 (2H, d, J = 8.4 Hz, Ar-H), 7.98 (2H, d, J = 8.4 Hz, Ar-H), 8.62 (1H, s, CH=N), 12.08 (1H, s, NH pyridone), 14.64 (1H, s, NH hydrazone); UV-Vis (EtOH) (λ_{max}/nm (log ε/mol^{-1}dm^{3}cm^{-1})): 457.0 (4.64).

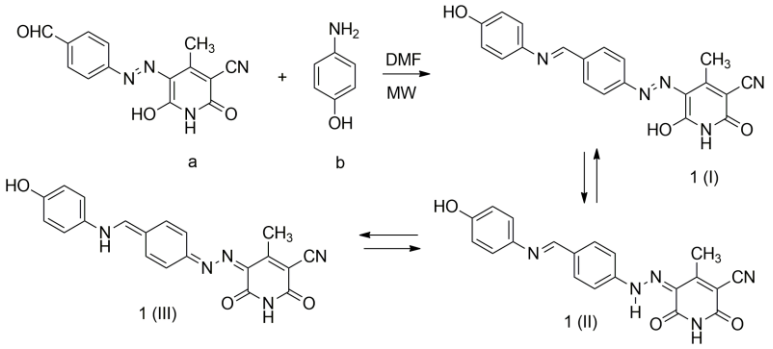

Fig 1. The microwave-assisted synthesis of novel azo-azomethine dye

2.2 Dyeing procedure

Viscose fabric (10 cm x 1.5 cm) was used as a substrate for dyeing. The dyeing of the viscose was performed under pH 8.5, at 60 °C for 90 min under constant shaking. The dyebath was prepared by dissolving the corresponding amount of dye (0.5% o.w.f., i.e. on the weight of fiber) in distilled water. After dyeing, the fabric was washed with warm distilled water and dried in the air at room temperature. To determine the colorimetric properties of the dyed viscose fabric, the colorimetric measurements (under illuminant D65 using the 10° standard observer) were performed using SF300 (Datacolor, USA) reflectance spectrophotometer with ultra-small area view (USAV). The color coordinates (L, a*, b*) of dyed viscose fabric were measured in the CIELab color space. In order to determine colorfastness to washing, the dyed fabric was washed in a bath containing 0.5% standard detergent at 40 °C for 30 min. After washing, the fabric was rinsed for 10 min, dried at room temperature for 24 h, and the colorimetric properties

were measured. The colorfastness to washing was evaluated based on the difference value (ΔE) between dyed fabric and dyed washed fabric [7].

2.3 Antioxidant assay

The antioxidant activity of the investigated dye was determined by the ABTS radical-scavenging assay, using the reported procedure [2]. The antioxidant activity of viscose fabrics was evaluated using ABTS test as well. In brief, a one-centimeter square sample of viscose fabric was added to a test tube containing 2 ml of freshly prepared ABTS radical in methanol solution and the reaction was continued at 25 °C for 30 min in the dark. The radical scavenging activity was evaluated using the absorbance of the solutions at 734 nm. The tests were performed in triplicate.

3. Results and discussion

3.1 Synthesis

Synthesized azo-azomethine dye can exist in different tautomeric forms such as imine-azo (I), imine-hydrazone (II) and amino-hydrazine (III), as it is presented in Fig. 1. The ATR-FTIR and NMR data of investigated dye indicate the existence of imine-hydrazone form in the solid state, as well as in DMSO-d_6 solution (Fig. 1, structure II). The N–H stretching vibrations of the hydrazone group appear at 3137 cm^{-1}. The broad band at 1652 cm^{-1} is ascribed to vibrations of carbonyl groups. The intensive band appearing at 1620 cm^{-1} is ascribed to the imine C=N group. The ^{1}H NMR spectrum contains the signal of hydrazone N–H group at 14.64 ppm, and the signal of imine CH=N group at 8.62 ppm confirming the existence of imine-hydrazone tautomeric form. An intense band appearing in the region 370-550 nm is ascribed to the intramolecular charge transfer (ICT) of the hydrazone tautomeric form [8].

3.2 Colorimetric properties and color fastness to washing of dyed viscose fabric

The color coordinates of dyed viscose fabric, before and after washing, were determined by using CIELab color space. The CIELab coordinates *L*, *a** and *b** were measured and presented in Table 1. From the value of *L* it can be noted that the given color is bright. The values of *a** and *b** propose that the color hues are shifted towards the redder and yellowish direction, respectively. Presented results show that investigated dye has an excellent affinity towards viscose fabric and gave pale rose color shade. The color difference value (ΔE) given in Table 1, shows a slight color change, indicating excellent washing fastness of investigated azo-azomethine dye.

Table 1. CIELab values of dyed viscose samples

Dyed viscose fabric	Before washing			After washing			ΔE
	*L*	*a**	*b**	*L*	*a**	*b**	2.17
	83.99	8.84	13.06	85.18	8.88	11.25	

3.3 Antioxidant properties

Antioxidant properties of azo-azomethine dye and viscose fabrics, before and after washing, have been evaluated by using the ABTS assay. The scavenging activity of the investigated dye was established and compared to the antioxidant properties of ascorbic acid. The test results have shown that azo-azomethine dye expressed excellent ability to scavenge the $ABTS^{\bullet+}$ radical cation with inhibition of 100%, comparing to the inhibition of ascorbic acid (100%). The

subjected dyed viscose fabrics exhibited very good antioxidant activity with inhibition of 56% for fabric before washing, and 28% for fabric after washing, comparing to the untreated viscose fabric (inhibition of 18%).

4. Conclusions

In this work, novel azo-azomethine dye has been synthesized using microwave technique, and its structure has been confirmed by ATR-FTIR, ^{1}H NMR and UV-Vis spectra. According to ATR-FTIR and NMR spectral data, the investigated dye exists in the imine-hydrazone form, in a solid state as well as in DMSO-d_6 solution. The azo-azomethine dye can be applied on viscose fabrics to produce pale rose color with excellent fastness to washing. Furthermore, the investigated dye has shown outstanding antioxidant properties and assayed dyed viscose fabrics exhibited very good free radical scavenging potential.

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