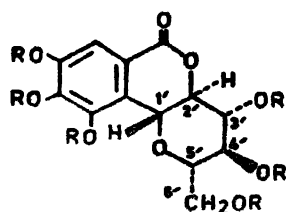


in this plant is also significant from chemotaxonomic viewpoint because of its close relationship with *Securinega* species as has been pointed out by some authors<sup>11</sup>.

### Experimental

The plant material was procured from United Chemical and Allied Products, Calcutta. The dried powdered roots (0.8 kg) was defatted with petroleum ether (b.p. 60–80°) and extracted with acetone. The acetone extract was concentrated to a small volume (150 ml) and left overnight. The resulting solid was crystallised from MeOH to afford colourless prisms of norbergenin, C<sub>15</sub>H<sub>14</sub>O<sub>9</sub>, m.p. 281°; *m/z* 314.0637 (C<sub>15</sub>H<sub>14</sub>O<sub>9</sub>), 195.0243 (C<sub>9</sub>H<sub>8</sub>O<sub>5</sub>) and 194.0201 (C<sub>9</sub>H<sub>8</sub>O<sub>5</sub>); <sup>1</sup>H nmr (MeOH-d<sub>4</sub>) δ 7.07 (1H, s, ArH) and 3.3–4.9 (7H, complex multiplet,



1; R=H  
1a; R=Ac

7 carbonyl hydrogens). *Norbergenin hexaacetate* (1a): C<sub>25</sub>H<sub>28</sub>O<sub>15</sub>, m.p. 212°; <sup>1</sup>H nmr (CDCl<sub>3</sub>) δ 1.99, 2.02, 2.04, 2.23, 2.25, 2.27 (3H, s, each 6-OAc), 3.72 (1H, d, *J* 8 Hz with fine splitting, H-5'), 4.03 (1H, d with fine splitting, *J* 11 Hz, H-6'), 4.23 (1H, d, *J* 11 Hz, H-6'), 4.32 (1H, t, *J* 8 Hz, H-2'), 4.79 (1H, d, *J* 8 Hz, H-1'), 5.06 (1H, t, *J* 8 Hz, H-4') and 5.40 (1H, t, *J* 8 Hz, H-3'). *Non-bergenin trimethyl ether*: (MeOH + CH<sub>2</sub>N<sub>2</sub>), m.p. 192°; identical with bergenin dimethyl ether in all respects (m.p., m.m.p., co-tlc). *Securinine*: the mother liquor of norbergenin was freed from solvent, stirred with aqueous citric acid (7%) and filtered. The filtrate was basified with NH<sub>4</sub>OH and extracted with EtOAc. The concentrated EtOAc extract on chromatography over silica gel yielded a pale yellow crystalline solid, C<sub>15</sub>H<sub>18</sub>NO<sub>2</sub> (*M*<sup>+</sup>, 217), m.p. 145°; [α]<sub>D</sub>—1283.33 (CHCl<sub>3</sub>); ν<sub>max</sub> (CHCl<sub>3</sub>) 1 810sh, 1 755, 1 640 cm<sup>-1</sup>; <sup>1</sup>H nmr (CDCl<sub>3</sub>) identical with reported values of securinine, *m/z* 217 (99.9%), 134 (100%), 106 (100%).

### Acknowledgement

One of the authors (S.K.) is grateful to Ministry of Health, New Delhi, for financial assistance.

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## Reactive Disperse Dyes. Synthesis of Sulphonylazido Group Reactive Disperse Dyes and their Application on Nylon and Polyester Fibers

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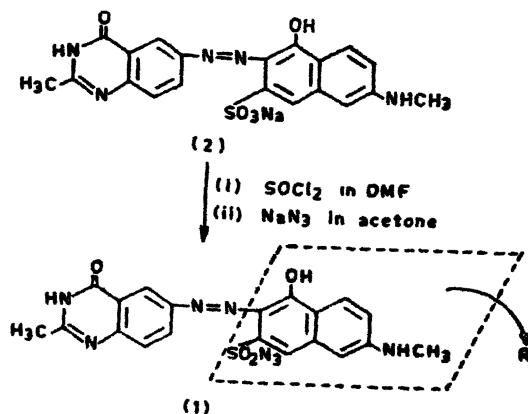
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Manuscript received 15 February 1988, revised 16 December 1988, accepted 23 May 1989

THE mechanism of the reaction of reactive dyes containing reactive units such as triazinylchloride or vinylsulphone involves nucleophilic substitution or nucleophilic addition<sup>1</sup>. As a result, these dyes will react with fibre such as cellulose, wool and nylon which contain nucleophilic groups and will be non-reactive towards polyester and polypropylene which are devoid of nucleophilic groups. Several azo and anthraquinone dyes and fluorescent whiteners containing sulphonylazido group for hydrophobic fibres<sup>2</sup> and also reactive disperse dyes have been prepared.

Several reactive disperse dyes have been involving nitrene intermediates<sup>4</sup> containing sulphonyl azido group(s) and involving sulphonylnitrene as the reactive intermediate. Sulphonylazides decompose thermally or photolytically to form sulphonylnitrenes which are readily inserted to various organic bonds including C—H bond<sup>5</sup>. These dyes were then dyed on nylon and polyester fibres by the usual disperse dyeing methods.

In our initial study, we have prepared several reactive disperse dyes containing sulphonyl azido group of the general structure 1 and dyed on nylon and polyester fibres by the usual disperse dyeing methods.



where, R is various coupling components having  $\text{SO}_2\text{N}_2$  group.

### Experimental

**2-Methyl-4-oxoquinazoline :** A mixture of *N*-acetylanthranilic acid (17.9 g, 0.1 mol) and acetic anhydride (36 ml) was refluxed for 30 min. The solid that separated on cooling was suspended in liquor ammonia (160 ml) and heated to  $100^\circ$  for 2 h. The white needles separated on cooling were filtered, dried and recrystallised from ethanol, (90%), m.p.  $235 - 36^\circ$ .

**2-Methyl-6-nitro-4-oxoquinazoline :** To 2-methyl-4-oxoquinazoline (6 g, 0.0375 mol) dissolved in concentrated sulphuric acid (20 ml) was added fuming nitric acid (10 ml) keeping temperature below  $75^\circ$ . The reaction mixture was poured on ice (200 g), filtered, washed with water and recrystallised from glacial acetic acid, (95%), m.p.  $299 - 300^\circ$ .

**2-Methyl-6-amino-4-oxoquinazoline :** 2-Methyl-6-nitro-4-oxoquinazoline (4.1 g, 0.02 mol) suspended in a solution of sodium sulphide (14.4 g, 0.06 mol) in water (75 ml) was refluxed for 2 h yielding a deep reddish brown solution. After cooling, diluting with water (75 ml) and strongly acidifying with hydrochloric acid, the solution was boiled for 20 min and filtered. Addition of sodium carbonate precipitated the pale yellow free amine which was recrystallised from ethanol, (87%), m.p.  $314 - 15^\circ$ .

**Diazonium chloride of 2-methyl-6-amino-4-oxoquinazoline :** 2-Methyl-6-amino-4-oxoquinazoline (3.50 g, 0.02 mol) was diazotised in the usual manner. The resulting diazo solution was used for the subsequent coupling reaction.

**Coupling of diazo solution with *N*-methyl *J*-acid :** *N*-Methyl *J*-acid (5.56 g, 0.02 mol) was suspended in water (25 ml) and dissolved to neutral pH with sodium carbonate solution (10%, w/v) to obtain a clear solution. The solution was cooled below  $5^\circ$  in an ice-bath. To it the above mentioned diazo solution was added dropwise with stirring maintaining the pH at 8 by simultaneous addition of sodium carbonate solution (1%, w/v) and the stirring continued for 3 h at  $0 - 5^\circ$ . The reaction mixture was

heated to  $60^\circ$  and sodium chloride was added until the colouring material was precipitated. It was stirred for 1 h, filtered, and the resulting solid was washed with a small amount of sodium chloride solution (5%, w/v) and dried to yield 2.

**Formation of sulphonyl chloride of dye 2 :** A mixture of the dye 2 (4.91 g, 0.01 mol) and chlorobenzene (40 ml) was heated under stirring and chlorobenzene (11 ml) was then distilled off to free the dye from the last traces of moisture. The reaction mixture was cooled to  $30^\circ$  and thionyl chloride (1.78 g, 0.015 mol) was added gradually, followed by the addition of DMF (0.365 g, 0.005 mol). The contents were stirred for 1 h at  $60^\circ$ . The temperature of the reaction mixture was then raised to  $95^\circ$  and stirred for further 1 h. The mixture was then cooled to room temperature and the separated sulphonyl chloride was washed with little petroleum ether and ice-cold water, (72 - 85%).

**Reaction of sulphonyl chloride of dye 2 with sodium azide :** The above sulphonyl chloride (4.88 g, 0.01 mol) was dissolved in acetone (111 ml) and stirred at room temperature, and to it sodium azide (0.78 g, 0.012 mol) dissolved in minimum amount of water (4 ml) and acetone (6 ml) was added gradually. The mixture was stirred for 0.5 h at room temperature and at  $50^\circ$  for 1 h. The reaction mixture was then diluted with water (126 ml) and stirred for 0.5 h and the resulting sulphonazide dye was washed with water and dried.

TABLE I—ANALYTICAL AND PHYSICAL DATA OF DYES

Dye no.	Coupling component (R)	Yield %	M.p. $^\circ\text{C}$	N % : Found/Calcd
D-1	<i>N</i> -Methyl- <i>J</i> -acid	88	281	24.06 (24.19)
D-2	<i>N</i> -Phenyl- <i>J</i> -acid	86	294	21.81 (21.99)
D-3	G-salt	81	272	25.81 (25.92)
D-4	R-salt	89	279	20.46 (20.58)
D-5	1-(4'-Sulphophenyl)-5-pyrazolone	78	263	27.85 (27.98)
D-6	1-(4'-Sulphophenyl)-3-methyl-5-pyrazolone	87	267	27.00 (27.09)
D-7	1-(4'-Sulphophenyl)-3-carboxy-5-pyrazolone	82	270	24.85 (24.45)
D-8	1-(2',5'-Dichloro-4'-sulphophenyl)-3-methyl-5-pyrazolone	85	301	23.51 (23.59)

**Application :** 2% shade on polyester. **Procedure.** The dye bath<sup>6</sup> was prepared as follows. A paste of weighed quantity of dye (40 mg) was prepared with dispersing agent Dadamol (40 mg), wetting agent Tween-80 (5 mg) and water (1 ml). To the paste was added water (99 ml) with stirring and pH adjusted to 4 using acetic acid.

In the dyeing process, the dye solution (100 ml) was added to a beaker provided with lid and screw cap. Before closing the lid and tightening the metal cap over the beaker, the wetted pattern of polyester

TABLE 2—PHYSICAL AND SPECTRAL DATA OF DYES

Dye no.	$R_f$	$\lambda_{max}$ nm	% Exhaustion		$\nu_{C=O}$ $cm^{-1}$	$\nu_{CH_2}$ $cm^{-1}$	$\nu_{N=N}$ $cm^{-1}$	$\nu_{SO_2N_2}$ $cm^{-1}$	$\nu_{NH}$ , $\nu_{HO}$ $cm^{-1}$
			Nylon	Polyester					
D-1	0.73	490	73	72	1 660	1 480	1 430	2 180	2 980–3 500
D-2	0.79	500	71	70	1 645	1 475	1 435	2 125	2 980–3 400
D-3	0.77	490	75	74	1 650	1 485	1 430	2 120	3 300–3 440
D-4	0.74	500	73	76	1 655	1 470	1 425	2 130	2 280–3 400
D-5	0.79	425	68	69	1 645	1 475	1 425	2 115	2 430–3 450
D-6	0.76	420	65	67	1 645	1 485	1 435	2 125	3 260–3 420
D-7	0.68	435	71	69	1 640	1 480	1 430	2 115	3 260–3 420
D-8	0.70	435	70	68	1 650	1 475	1 425	2 130	3 300–3 440

was rolled properly and dropped in to the beaker. The beaker was then placed vertically and the rotatory carrier inside the tank was allowed to rotate in the glycerin bath whose temperature was raised at rate of 2° per min up to a final temperature at 130°. The dyeing was continued for 60 min at 130° under pressure. After cooling over a period of 1 h, the beaker was removed from the bath and washed with water. The pattern was washed several times with cold water. The above dyed pattern was further treated with a solution of detergent (0.2 g) and sodium carbonate (0.1 g) in water (100 ml) at 80° for 30 minutes, and after washing thoroughly water, it was dried.

**2% shade on nylon :** The materials used were as follows : Nylon fabric, 2 g ; amount of dye solution under study at pH 3, 40 ml (0.1%, w/v) ; MLR, 1 : 30 ; total volume of dye bath, 60 ml. The dye bath<sup>7</sup> with MLR 1 : 30 was adjusted to pH 3 using acetic acid. The sample of nylon fabric was introduced in the dye bath at room temperature and its temperature slowly raised to 100° in 15 minutes. The fabric was worked up in dye bath at 100° for 1 h and then washed with warm water, cold water and dried.

Reactive disperse dyes containing sulphonyl azido group were separated on tlc using n-butanol–pyridine–water (25 : 25 : 15) solvent system. The results are given in Table 2.

The electronic spectra (DMF) were determined using a Bausch and Lomb Spectronic-20 spectrophotometer using concentration of dye solution  $2 \times 10^{-3}$  M (Table 2).

The percentage exhaustion of the dyes were performed using the standard procedure. The results are given in Table 2.

#### Acknowledgement

The authors are thankful to South Gujarat University for facilities and to Mantra Educational Institute, Surat, for dyeing facilities.

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### Analytical Reagent TQA—Photometric Determination of Copper(II) in Alkaline Medium and Trace Analysis in Steel†

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Manuscript received 1 September 1987, revised 12 September 1988, accepted 17 May 1989

THE paper describes the synthesis and use of *N*-(phenyl)-2-thioquinaldinamide as a spectrophotometric reagent for the determination of trace amount of copper(II) in synthetic materials.

#### Experimental

Copper(II) solution was prepared by dissolving pure electrolytic grade Cu-wire in aqua regia and sulphuric acid and standardised iodometrically.

**Procedure :** To an aliquot containing 100  $\mu$ g ml<sup>-1</sup> of copper(II), 2 M KOH (1.5 ml) was added to adjust the pH to 11.0. Then a 0.1% alcoholic reagent solution (5 ml) was added and the volume made up to 25 ml. The absorbance of the violet complex was measured at 525 nm after 2–3 min against the reagent blank.

#### Results and Discussion

The copper(II) complex showed absorption maximum at 520–530 nm at pH 11.0. The complex showed constant absorbance for 1.5–6.0 ml of 0.1% reagent. A 5 ml of 0.1% solution was always used. The absorbance was constant upto 4.0 ml of 2 M KOH and measured at pH 11.0. The complex

† Presented at 75th Indian Science Congress, Pune, 1988.