

## CHALCONES - A NEW CLASS OF POTENTIAL NON-AZO DYES

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## ABSTRACT

Five substituted chalcones have been synthesized by Claisen-Schmidt condensation of substituted acetophenones and substituted benzaldehydes in the presence of a base by conventional and microwave assisted method. They have been characterized by spectral data and evaluated as non-azo dyes for dyeing of silk fabric using metallic and natural mordants and their combination. Optimization of different dyeing conditions as well as washing and light fastness of some selected dyed samples has also been examined.

**Keywords:** Azo-dyes, Synthetic chalcones, Optimization of dyeing conditions, Colour fastness.

## INTRODUCTION

Majority of synthetic dyes used in dyeing of textile fibres are mainly azo dyes which require huge quantity of carcinogenic aryl amines and naphthols in their synthesis. The effluents coming out of the synthetic dyes factories are not only harmful to the flora and fauna of the region but also to the human being living in those areas as well as to the user<sup>1</sup>. The national and international awareness about depletion of natural resources, ecological balance, pollution problems developed due to use of hazardous chemicals have forced the scientists to develop safer alternate to azo dyes. The presence of toxic chemicals including synthetic dyes has been restricted to specified limit under "EC control of substances" hazardous to health Act 1989 and published a red list of twenty banned amine based dyes<sup>2</sup>. This led Germany to ban the imported textile fibres dyed with azo dyes during April 1996. Since then the use of azo dyes has also been banned in USA, European countries as well as in Indian Sub-continent<sup>3</sup>. As a result of health hazard created by these synthetic azo dyes, there is again a great demand to revive the age old art of dyeing with natural dyes because they are non-toxic and non-carcinogenic in comparison to synthetic azo dyes<sup>4</sup>. There is no doubt that natural dyes are good alternate to synthetic azo dyes but due to high cost involved in isolation and separation of natural dyes, meager natural resources to cultivate dye yielding plants, inadequate degree of fixation and fastness properties forced the scientists to synthesize non azo dye such as anthraquinones, flavonoids and chalcones etc. Chalcones<sup>5</sup> are open chain analogues of flavonoids in which the two aromatic rings A and B are joined by three carbons,  $\alpha$ ,  $\beta$ -unsaturated carbonyl system (fig1).

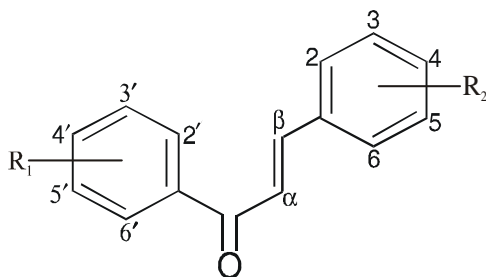


Fig. 1: Chalcone molecule

They are precursors in flavonoids biosynthesis. Besides, they play an ecological role in nature, in relation to plant colour. These bright yellow coloured compounds are found in many plant organs, and in some families they contribute significantly to the corolla pigmentation<sup>6</sup>. No systematic work has been carried out to use synthetic substituted chalcones as non-azo dyes. Thus the present work has been under taken to development of substituted chalcones

as cheap, safe and easy to prepare alternate to replace existing costly natural and toxic azo dyes.

## MATERIAL AND METHODS

## Chemicals and apparatus

The substituted acetophenones (3-nitro, 4-nitro, 4-amino) and substituted benzaldehydes (4-hydroxy, 4-hydroxy-3-methoxy, 4-dimethylamino) were employed for the synthesis of substituted chalcones. Melting points were determined in Thomas Hoover melting point apparatus and are uncorrected. UV spectra were taken by using Perkin Elmer Lambda 15 UV/VIS spectrometer. IR spectra of the corresponding compounds were recorded on a Shimadzu 8201 PC spectrometer (4000-400  $\text{cm}^{-1}$ ) by using KBr plates and absorption bands are reported in  $\text{cm}^{-1}$ . The  $^1\text{H-NMR}$  spectra were recorded on Bruker DRX-300 (300 MHz FT NMR) spectrometer in deuterated methanol using TMS as internal standard and chemical shift are expressed in  $\delta$  (ppm) values. The FAB mass spectra were recorded on a JEOL S X 102 mass spectrometer using Argon/Xenon (6 KV, 100 mA) as the FAB gas. All reactions were monitored by thin layer chromatography carried out on 0.2 mm silica gel G plates using suitable solvent systems. The purity of the compounds was ascertained by thin layer chromatography. All the chemicals used were obtained from E-merck/ Glaxo Ltd, Mumbai. The reagents and solvents such as hexane, benzene, chloroform, acetone, ethanol and methanol used were of LR and AR grade.

## Synthesis of substituted chalcones

## (i) Conventional method

A mixture of substituted acetophenone (0.1 mole) and substituted benzaldehyde (0.1 mole) dissolved in 250 ml of ethanol was taken in a round bottom flask, kept in ice bath. The condensation was affected by adding of a strong solution of KOH (75 c.c., 12 N) drop by drop using constant stirring. The reaction mixture was left in the same ice bath for 30 minutes and then refluxed for 9-12 hours. The completion of reaction was monitored by using silica gel thin layer chromatography (TLC) plates using mobile phase. The resultant mixture was cooled, neutralized with ice chilled dilute HCl (5%), stirred, when precipitate of crude substituted chalcone obtained which was filtered, washed thoroughly with ice cold distilled water, till free from acid<sup>[7,8]</sup>. The crude chalcone was purified and crystallized from methanol.

## (ii) Microwave induced method

The condensation of substituted acetophenone (0.1 mole) with substituted benzaldehyde (0.1 mole) was carried out using ethanol as energy transfer medium in the presence of base (KOH) in the specially designed conical flask fitted with calcium chloride guard tube to absorb solvent vapors for 10 to 50 seconds at 450 watts

microwave power. The reaction mixture was irradiated in 10 seconds increment. The progress of the reaction was monitored by silica gel thin layer plates using chloroform: acetone (8:2) solvent systems as well as by the appearance of colored product during

reaction. After completion of reaction, the work up of the product was carried out according to the procedure similar to conventional method. The experimental conditions and physical properties of all substituted chalcones are shown in Table 1.

**Table 1: Comparison of reaction time and yield of chalcone dyes prepared by conventional method (CM) with microwave induced method (MwIM)**

Chalcone Dyes	R <sub>1</sub>	R <sub>2</sub>	Reaction time		% Yield		M.P. (°C)	Colour
			CM (Hrs)	MwIM (Sec)	CM	MwIM		
Dye I	4'-NO <sub>2</sub>	4-OH	9	20	73	90	84	Yellow
Dye II	4'-NO <sub>2</sub>	4-OH-3-OCH <sub>3</sub>	10	20	70	85	150	Yellow
Dye III	4'-NH <sub>2</sub>	4-OH-3-OCH <sub>3</sub>	12	30	65	82	190	Yellow
Dye IV	4'-NH <sub>2</sub>	4-N(CH <sub>3</sub> ) <sub>2</sub>	9	50	75	88	168	Reddish orange
Dye V	3'-NO <sub>2</sub>	4-OH-3-OCH <sub>3</sub>	10	30	68	86	170	Yellow

### Preparation of dye solutions

First of all, different amounts of all five dyes that are 0.50, 1.00, 1.50 and 2.00 gm were dissolved in 0.1 to 0.4 %wt/V in slightly acidic water (pH 5-6) respectively. The colour solutions were used for dyeing of silk samples.

### Fabric for dyeing

A pure white silk purchased locally from Gandhi Ashram, Agra, was soaked in distilled water then scoured in detergent solution to remove fatty impurities, washed with distilled water and dried under shade and ironed. The silk was cut into the pieces of size (10 × 4 cm) and used for mordanting with natural and metallic mordants before dyeing with dyes.

### Mordanting<sup>9</sup>

The metallic mordants used were Mohr's salt, Copper Sulphate, Nickel Sulphate, Stannous Chloride and Cobalt Sulphate. The concentrations used for metallic mordants were 0.5, 1.0, 1.5, 2.0 gm/100 ml of water. The required amount of mordants were dissolved in distilled water and stirred till a clear solution was obtained. The natural mordants used were barks of Walnut (*Juglans Regia*), bark of pomegranate (*Punica Granatum*), Acacia Catechu (*Mimosaceae*), Gooseberry (*Emblica Officinalis*), and Black Catechu (*Acacia Chundra*). The concentrations used for natural mordants were 0.5, 1.0, 2.0, 2.5 gm/100 ml of water. They were dissolved in water and boiled at 80-90 °C for one to two hours till the complete extraction, then cooled and filtered. The clear filtrate used for mordanting of silk samples.

Silk pieces of size 10 × 4 cm were added to the dye bath. The mordanting was carried out in a water bath at 70-80 °C for one to one and half hours with constant stirring till even distribution of mordants takes place. It was then dried at room temperature. The different concentrations of mordants were employed to optimize mordant concentration.

The silk samples were also pre-mordanted with the combination of natural and metallic mordants. First of all, silk pieces added to solution of natural mordants at 70-80 °C for one hour with constant stirring and then dried at room temperature. Next day they were subjected to mordanting with metallic mordants. Samples were dried at room temperature and used for dyeing.

### Methods of mordanting

In present study pre-mordanting method was used prior to dyeing. First of all, silk samples were mordanted at 80-90 °C for 1 hour with constant stirring for even distribution of mordants over the silk pieces then allowed to dry at room temperature. Later these samples were dyed in 1.00% concentration of dyes I and V while 1.50%

concentration of dyes II, III and IV used for dyeing of silk at 80-90 °C for 1 hour.

### Dyeing times

In order to optimize dyeing time mordanted silk samples were dyed with different chalcone dyes for different time periods (30, 60, 90 and 120 minutes) keeping other parameters as constant.

### Dyeing of silk fabric

Pre-mordanted silk samples of size (10 × 4 cm) were immersed in beaker containing different concentrations (0.50, 1.00, 1.50, 2.00 gm/100 ml) of chalcone dyes were placed in dye bath at 90 °C for few minutes followed by simmering at 70-80 °C for 30, 60, 90, 120 minutes. The dye solutions were constantly stirred to obtain even shades. The samples removed, washed with distilled water and dried in air at room temperature.

### Light and washing fastness of dyed silk samples<sup>10,11</sup>

Some silk samples were subjected to washing fastness tests in a Launder-O-Meter and the change in colour of dyed samples were evaluated as per IS: 786 BS-1956 while the degree of staining has been determined by IS: 769 BS-1956 methods. Light fastness of dyed samples was also taken under consideration as per ISO 105- B02-1981 under Xenon arc lamp of correlated colour temperature of 5500 to 6500 K. Standard patterns of blue wool cloth ranging in light fastness rating no.1 (very low light fastness) to rating no.8 (very high light fastness) and gray scales were used to determine change in colour of the dyed silk samples. All these testing were carried out at SASMIRA (The Synthetic & Art Silk Mills' Research Association), Mumbai.

## RESULT AND DISCUSSION

Each of the five chalcones synthesized by conventional method as well as a rapid and efficient microwave induced method showed characteristic colour reactions of chalcones. Also the compound synthesized showed the following physical characteristic and spectral data

### (Dye I) 4-Hydroxy-4'-nitrochalcone

m.p. 84°C; UV (MeOH)  $\lambda_{max}$ (nm) 265, 352; FTIR (KBr)  $\nu_{max}$  (cm<sup>-1</sup>) 3201(-OH), 1456, 1355, 1159 (-NO<sub>2</sub> symm. strec., assym strec., C-N strec.), 1687 (-CO-CH=CH-); <sup>1</sup>H<sub>1</sub>-NMR (CD<sub>3</sub>OD)  $\delta$ (ppm) 7.41 (d,1H, H<sub>a</sub>), 7.52 (d,1H, H<sub>b</sub>); FAB-MS at m/z 269 [M<sup>+</sup>], 268 [M<sup>+1</sup>], 241, 150, 147, 119, 107, 77.

### (Dye II) 4-Hydroxy-3-methoxy-4'-nitrochalcone

m.p. 150°C; UV (MeOH)  $\lambda_{max}$ (nm) 240, 324, 390; FTIR (KBr)  $\nu_{max}$ (cm<sup>-1</sup>) 3245 (-OH), 2945 (-OCH<sub>3</sub>), 1513, 1325, 1126 (-NO<sub>2</sub> symm. strec., assym strec., C-N strec.), 1639 (-CO-CH=CH-); <sup>1</sup>H<sub>1</sub>-NMR (CD<sub>3</sub>OD)  $\delta$ (ppm) 7.20 (d,1H, H<sub>a</sub>), 7.55 (d, 1H, H<sub>b</sub>), 3.96 (s, 3H,-

OCH<sub>3</sub>), 9.76 (s, 1H, -OH); FAB-MS at m/z 299 [M<sup>+</sup>], 298 [M<sup>+1</sup>], 177, 150, 149, 137, 77.

#### (Dye III) 4'-Amino-4-hydroxy-3-methoxychalcone

m.p.190°C; UV (MeOH) λ<sub>max</sub>(nm) 230, 326, 373; FTIR (KBr) ν<sub>max</sub>(cm<sup>-1</sup>) 3356 (-NH<sub>2</sub>), 3230 (-OH), 2867 (-OCH<sub>3</sub>), 1648 (-CO-CH=CH-); <sup>1</sup>H<sub>1</sub>-NMR (CD<sub>3</sub>OD) δ(ppm) 7.25 (d,1H, H<sub>α</sub>), 7.65 (d,1H, H<sub>β</sub>), 3.33 (s, 2H, -NH<sub>2</sub>), 3.96 (s, 3H,-OCH<sub>3</sub>), 9.77 (s,1H, -OH); FAB-MS at m/z 269 [M<sup>+</sup>], 268 [M<sup>+1</sup>], 177, 149, 137, 120, 77.

#### (Dye IV) 4'-Amino-4-dimethylaminechalcone

m.p.168°C; UV (MeOH) λ<sub>max</sub>(nm) 418, 328; FTIR (KBr) ν<sub>max</sub>(cm<sup>-1</sup>) 3387 (-NH<sub>2</sub>), 2921, 1348 (-N(CH<sub>3</sub>)<sub>2</sub> strec.), 1642 (-CO-CH=CH-); <sup>1</sup>H<sub>1</sub>-NMR (CD<sub>3</sub>OD) δ(ppm) 7.54 (d,1H, H<sub>α</sub>), 7.73 (d,1H, H<sub>β</sub>), 3.33 (s, 2H, -NH<sub>2</sub>), 3.0 (s, 6H, -N(CH<sub>3</sub>)<sub>2</sub>); FAB-MS at m/z 266 [M<sup>+</sup>], 265 [M<sup>+1</sup>], 174, 146, 134, 120, 77.

#### (Dye V) 4-Hydroxy-3-methoxy-3'-nitrochalcone

m.p. 170°C; UV (MeOH) λ<sub>max</sub>(nm) 220, 312, 390; FTIR (KBr) ν<sub>max</sub>(cm<sup>-1</sup>) 3248(-OH), 2933 (-OCH<sub>3</sub>), 1514, 1328, 1160 (-NO<sub>2</sub> symm. strec., assym strec., C-N strec.), 1690 (-CO-CH=CH-); <sup>1</sup>H<sub>1</sub>-NMR (CD<sub>3</sub>OD) δ(ppm) 8.12 (d,1H, H<sub>α</sub>), 8.33 (d,1H, H<sub>β</sub>), 3.86 (s, 3H,-OCH<sub>3</sub>); FAB-MS at m/z 299 [M<sup>+</sup>], 298 [M<sup>+1</sup>], 177, 150, 149, 134, 77.

From spectral data it is evident that all the chalcones showed the presence of keto vinyl group (-CO-CH=CH-) in the range of 1639 to

1690 cm<sup>-1</sup>, the presence of -OH, -OCH<sub>3</sub>, -NO<sub>2</sub>, -NH<sub>2</sub> and -N(CH<sub>3</sub>)<sub>2</sub> were also characterized by IR spectrum. <sup>1</sup>H<sub>1</sub>-NMR spectrum showed a pair of doublets corresponding to vinylic H<sub>α</sub> and H<sub>β</sub> in the range of 7.20 to 8.12 ppm and 7.52 to 8.33 ppm respectively. All the chalcones showed strong mass peak followed by [M-1] peak.

Optimizations of concentrations of all chalcones dyes were determined on the basis of % absorbance of dye on fibre surface by using SL-171-Elico spectrophotometer. For Dye I and V, the optimum concentration was found 1.00 gm/100 ml water while on other hand optimum concentration was found 1.50 gm/100 ml of water for dye II, III and IV. Initial experiments have indicated that pre-mordanting technique gave better results as compared to post and simultaneously mordantings. Thus for all the silk samples were mordanted by the metallic as well as natural mordants using pre-mordanting method. The optimum concentration was found to be 2% i.e. 2gm/100ml water and 1% i.e. 1gm/100ml for natural and metallic mordants respectively. As regard to optimization of dyeing time, one hour dyeing gave the best result for silk samples.

Throughout the dyeing process, varieties of brilliant shades of different colours viz. yellow, orange, reddish orange, rust, brown have been obtained with all chalcones dyes. Out of them some selected samples were subjected to washing as well as light fastness. Fair to moderate washing and light fastness were observed for pre-mordanted silk samples dyed with chalcone dyes (Table 2).

Table 2: Rating for colour fastness of mordanted silk samples dyed with dyes II, III AND IV

Treatment	Concentration Of mordants	Rating for washing fastness			Rating for light fastness***
		Change in shade*	Staining on cotton**	Staining on silk**	
<b>Dye II</b>					
Without mordant	-	1	4	3-4	3
Barks of Walnut	2%	1-2	3-4	3	3-4
Barks of Walnut+FeCl <sub>3</sub>	2% + 1%	2-3	4	4	3-4
<b>Dye III</b>					
Without mordant	-	1	3-4	4	3
Acacia Catechu	2%	1-2	3	2-3	3-4
FeCl <sub>3</sub>	1%	3	2-3	2-3	3-4
CuSO <sub>4</sub>	1%	2	3-4	2-3	3-4
<b>Dye IV</b>					
Without mordant	-	1	4	4	3-4
Barks of Walnut	2%	1	4	4	3-4
Acacia Catechu + CuSO <sub>4</sub>	2% + 1%	1	4-5	4	3
Barks of Walnut+FeCl <sub>3</sub>	2% + 1%	1-2	4-5	4	3-4

\*Rating for washing varies from 1 to 5; where 1= poor fastness, 5= excellent fastness. \*\* 5= no staining, 4= slight stained, 3= noticeably stained, 2= considerably stained, 1=heavily stained. \*\*\* Rating for light varies from 1 to 8; where 1= very poor, 2= poor, 3= fair, 4= fairly good, 5= good, 6= very good, 7= best, 8= excellent.

## CONCLUSION

It may be concluded that varieties of beautiful shades were obtained from the synthesized chalcones having fair to moderate fastness to light and washing. Thus chalcones may be used as potential non-azo dyes for dyeing of silk fabric. Thus they can be used as an alternative to azo dyes which are carcinogenic and banned in majority of countries of the world. The data generated during the work may be used as basis for studying the economics and viability of synthesis of chalcones dyes on commercial scales.

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