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Dyeing cotton, wool and silk with *Hibiscus mutabilis* (Gulzuba)

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Abstract

Hibiscus mutabilis (Gulzuba)/Cotton rose/ belongs to family Malvaceae produces natural dye which has been used for dyeing textiles. Aqueous extract of Gulzuba flowers yield shades with good fastness properties. The dye has good scope in the commercial dyeing of cotton, silk for garment industry and wool yarn for carpet industry. In the present study dyeing with gulzuba has been shown to give good dyeing results. Pretreatment with 2–4 % metal mordants and keeping M:L ratio as 1:40 for the weight of the fabric to plant extract is optimum showing very good fastness properties for cotton, silk and wool dyed fabrics.

Keywords: Hibiscus mutabilis; natural dye; cotton; silk; wool; commercial dyeing

1. Introduction

Hibiscus mutabilis/Gulzuba/Cotton rose is a large shrub or small multi-stemmed tree that grows to 15 ft (4.6 m) high with about a 10 ft (3 m) spread. It is neither a true hibiscus nor a rose (it is in Malvaceae, the hibiscus family). *H. mutabilis* is downright conspicuous when in full bloom starting in late winters. The flowers open pure white and change color over a 3-day period until they are deep pink and then as they die, assume a dark "blue-pink" hue. The most notable characteristic of this flowering shrub is that flowers of 3 distinct colors appear on the bush simultaneously, as the blooms' color cycle is independent of one another. Single and double flowered varieties are available, both having quite large blossoms that are 3–5 in (8–13 cm) across. After flowering, a round, hairy capsule forms which dries and releases fuzzy seeds, a trait that inspired one of the plants common names, rose cotton as the buds resemble the ball of that famous member, Gossypium, also of the hibiscus family. The large leaves are 5–7 in (13–18 cm), bright green, hairy on the undersides and deeply lobed. They impart a coarse texture that gives the plant a distinctive eye-catching appeal. There is always a great demand in garden centers for the cotton rose when it is in full bloom, for it is one of the most imposing and unusual of flowering trees. Little to no care is required. This shrub truly takes care of itself and is adaptable to most locations and soil conditions and under sun or light shifting shade. This shrub thrives on regular watering but this is optional as it is very drought tolerant. Propagated by cuttings, Gulzuba is easy to root.

1.1. Color changes in the petals

The petals of this plant change color [1–3] from ivory white in the morning to light rose at noon and pink-red in the evening. Examination of petals at the 3 periods showed

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that the flavonol glycosides in all 3 were isoquercitrin, hyperoside, rutin, quercetin 4′-glucoside and quercimeritrin, and the free aglycon was quercetin. There was no anthocyanin in the morning batch but in the other 2 there were cyanidin 3,5-diglucoside and cyanidin 3-rutinoside-5-glucoside, with cyanidin as the free aglycon. Studies have shown that the content of total anthocyanin in the evening was 3-fold greater than that at noon. Since during the day there was no decrease in flavonols, the anthocyanins were evidently synthesized independently. When opening in the morning, flowers of *H. mutabilis* appear white or ivory. The flower color changes to red by late afternoon due to the accumulation of the anthocyanin cyanidin 3-sambubioside. At the onset and during the rapid phase of pigment accumulation, phenylalanine ammonia-lyase (PAL) activity in the petals increases rapidly to 7 times its initial level and then decreases while the flower senesces. In excised petals, the PAL inhibitor L-α-aminooxy-β-phenylpropionic acid suppresses pigment formation and causes the accumulation of phenylalanine. Anthocyanin synthesis depends, therefore, on the de novo production of cinnamic acid. Two kinds of anthocyanins in the red petals of *H. mutabilis* were identified as cyanidin 3-xylosylglucoside (ilicicyanin) and cyanidin 3-monoglucoside (chrysanthemin), which were present in the ratio 8:2. The hydrolyzed petal extracts from both white and red flowers contained quercetin and kaempferol in the ratio 7:3. The white petals produced a considerable amount of anthocyanins, when they were detached and floated on water in the light and (or) dark. Metabolic inhibitors inhibited markedly the pigment production in the detached petals, and sucrose promoted it to some extent.

2. Materials and methods

2.1. Materials

2.1.1. Flower color chosen

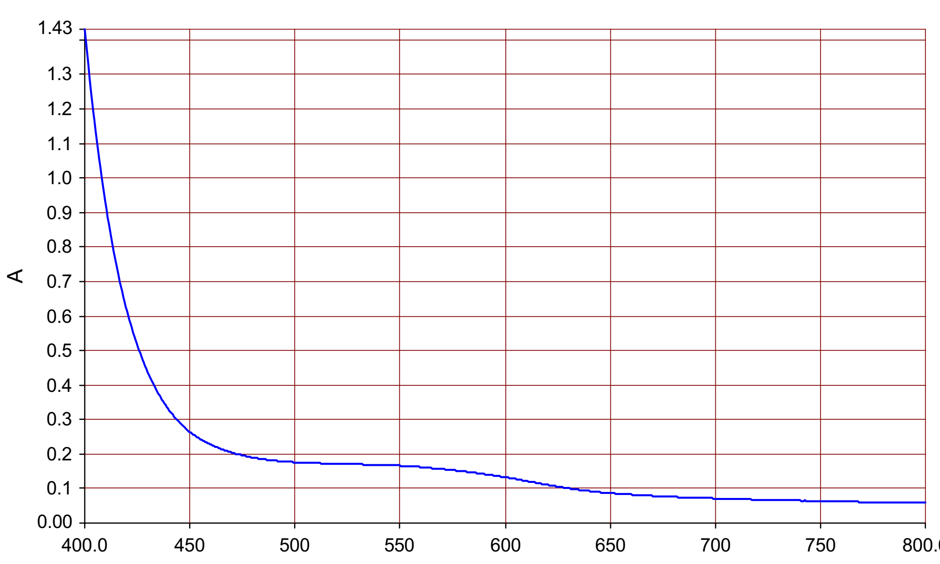
Dark pink variety of *H. mutabilis*/Gulzuba flowers were collected from the IIT Kanpur horticulture department. The plant grows in full Sun in a rich amended soil for full bloom. The blooming period is February–May. The pigment obtained from Gulzuba has good coloring capacity. It is thermostable, thus is also suitable for conventional dyeing where the bath temperature ranges from 60 to 90 °C.

2.1.2. Studies on cotton, silk and wool

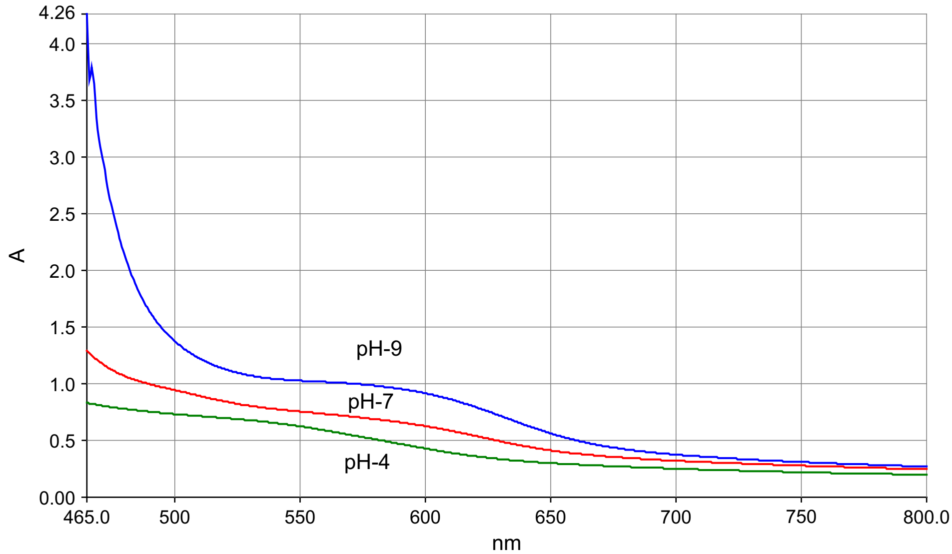
Bleached cotton was used for dyeing. Khadi silk was used. Commercially bleached wool yarn supplied by Jaypee (pure new wool) was used for dyeing.

2.1.3. Chemicals used

Metallic salts such as alum, stannic chloride, stannous chloride were supplied by S.D. Fine and ferrous sulphate was supplied by Loba Chemie.



Graph 1. Visible spectra of *Hibiscus mutabilis* flowers.



Graph 2. Visible spectra of *Hibiscus mutabilis* at different pH.

2.2. Methods

2.2.1. Extraction of colorant

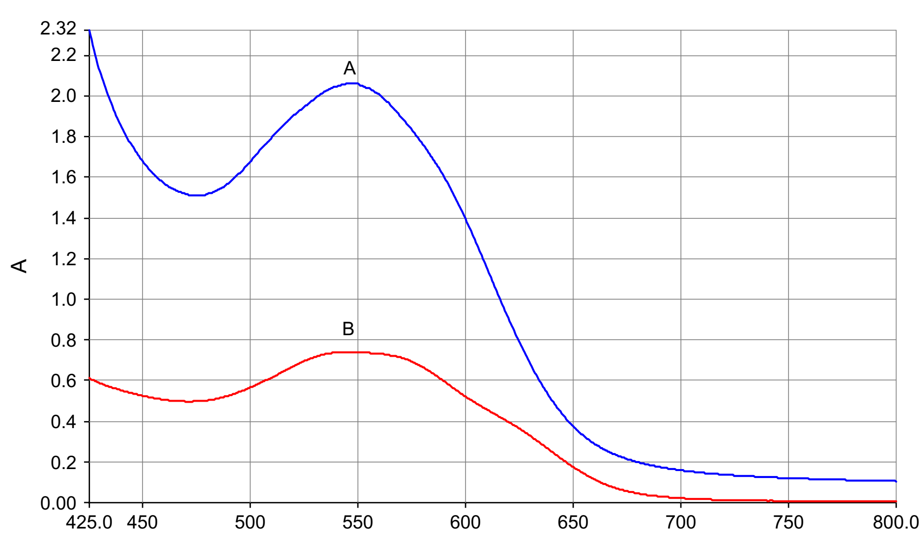
Flowers from plant source were crushed and dissolved in distilled water and allowed to boil in a beaker kept over water bath for quick extraction for 3 h. All the colors were extracted from the flowers by the end of 3 h. The solution was filtered for further use. The colorant showed one major peak, λ_{max} at 585 nm in the visible region. The visible spectrum of aqueous extract of fresh flowers is shown in Graph 1. The extract shows slight changes in different pH as shown in Graph 2. At pH 4, 7 and 9, the λ_{max} was at 585.64 nm, however, their absorbance were different – 0.48, 0.67 and 0.96, respectively.

2.2.2. Scouring of cotton, silk and wool

Cotton fabric, silk fabric and wool yarn were washed with a solution containing 0.5 g/L of sodium carbonate and 2 g/L of non-ionic detergent (Labolene) at 40–45 °C for 30 min, keeping the material to liquor ratio at 1:50. The scoured material was thoroughly washed with tap water and dried at room temperature. The scoured material was soaked in clean water for 30 min prior to dyeing or mordanting.

2.2.3. Mordanting

Vegetable dyes require chemical in the form of metal salts to produce an affinity between the cotton, silk fabrics and wool yarn and the pigments, these chemicals are known as mordants. Accurately weighed cotton, silk or wool sample was



Graph 3. Dye uptake from fresh flower extract.

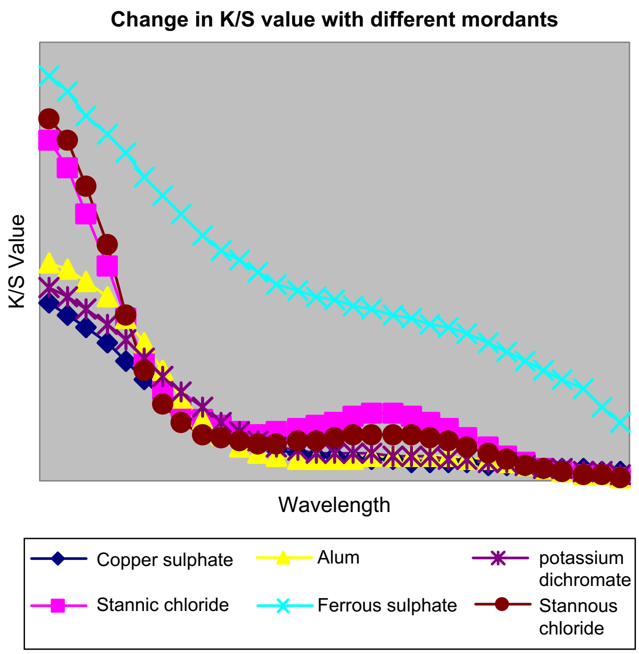


Fig. 1. Change in *K/S* values with different mordants.

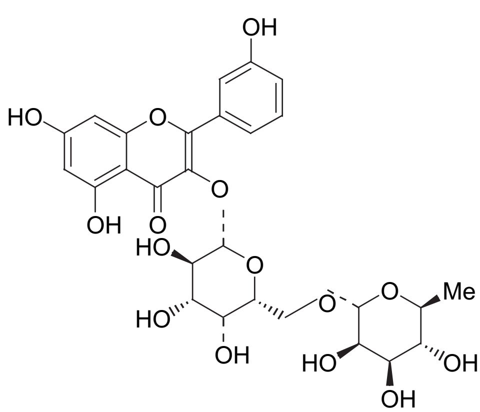
treated with different metal salts, only pre-mordanting with metal salts was carried out before dyeing. The mordant was dissolved in water to make the liquor ratio 1:50. The wetted sample was introduced into the mordant solution and then it was brought to heating. Temperature of the dye bath was raised to 60 °C over half an hour and left at that temperature for another 30 min. The dyed material was then rinsed with water thoroughly, squeezed and dried. It is suggested that mordanted cotton and wool should be used immediately because some mordants are very sensitive to light.

2.2.4. Dyeing

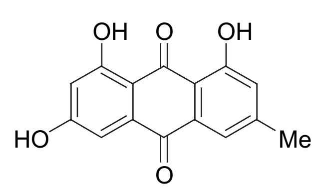
The cotton, silk, as well as wool yarn were dyed with dye extract, keeping *M*:*L* ratio as 1:40, however, for cotton dyeing it was used directly while in the case of silk and wool dyeing the pH was maintained at 4 by adding buffer solution (sodium acetate and acetic acid). The dye extract was prepared by adding 4 g dye powder in 100 ml water (*M*:*L* :: 1:40). The prepared fabric was dipped in the dye bath for 1 h. The dyed material was washed with cold water and dried at room temperature, it was then dipped in brine for dye fixing. The color strength was determined colorimetrically using Premier Colorscan at the maximum wavelength of the natural colorant (Graph 3).

2.2.5. Measurement of color strength [1]

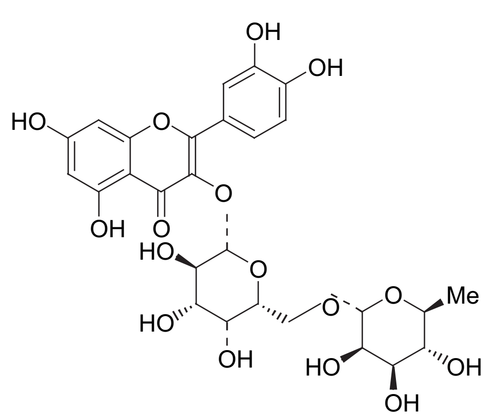
The color yield of both dyed and mordanted samples was evaluated by light reflectance measurements using Premier Colorscan machine.



Kaempferol-3-O-β-D-robinobioside



Emodin



Rutin

Table 1
Different pre-mordants, color obtained *X*, *Y*, *Z* and *L**, *a**, *b** values for dyed cotton fabric with *Hibiscus mutabilis*

Pre-mordanting	Color obtained	*X*	*Y*	*Z*	*L**	*a**	*b**
Alum	Bright green	70.62	74.68	81.76	89.24	−0.34	−1.18
Ferrous sulphate	Dark green	5.45	5.84	5.28	29.02	−1.01	4.33
Stannous chloride	Purple	9.91	9.93	11.99	37.72	3.95	−3.68
Copper sulphate	Moss green	9.47	10.11	5.13	38.04	−0.91	20.61
Potassium dichromate	Green	28.81	29.95	18.05	61.61	1.68	23.43
Stannic chloride	Light purple	15.16	16.39	16.09	47.48	0.48	3.21

The color strength (*K*/*S* value) was assessed using the Kubelka–Munk equation:

$$K/S = (1-R)^2/2R$$

where *R* is the decimal fraction of the reflectance of dyed yarn.

Different mordants show change in *K*/*S* values as shown below in Fig. 1.

3. Chemical composition of the colorant

Petals of *H. mutabilis* (0.5 kg) were extracted twice with a Me_2CO–H_2O (1:1) mixture (5 L) at 50–55 °C for 20–25 min, the extract was filtered, and Me_2CO was distilled off to give dry product (60 g) containing 12–13% red pigment. Preliminary analysis showed that the pigment contained [4,5] nonacosane, β-sitosterol, betulinic acid, hexyl stearate, stigmasta-3,7-dione, stigmasta-4-ene-3-one tetratriacontanol quercetin, and kaempferol. Isolation and purification were carried out on silica gel or polyamide column chromatography. The constituents were identified by physicochemical properties and spectral analysis. Ten compounds were obtained, eight of them were determined as tetracosanoic acid, β-sitosterol, daucosterol, salicylic acid, emodin, rutin, kaempferol-3-*O*-β-rutinoside, kaempferol-3-*O*-β-robinobioside, and kaempferol-3-*O*-β-D-(6-*E*-*p*-hydroxycinnamoyl)-glucopyranoside. All compounds were isolated from the plant for the first time except β-sitosterol and salicylic acid. The new flavonol glucoside quercetin 3-sambubioside [6] (**I**), as well as isoquercitrin, hyperin, guaijaverin, and a compound yielding kaempferol, glucose, galactose, and xylose on acid hydrolysis were isolated from the ethyl acetate extract of pink petals of *H. mutabilis*.

Table 2
Different pre-mordants, color obtained *X*, *Y*, *Z* and *L**, *a**, *b** values for dyed wool yarn with *Hibiscus mutabilis*

Pre-mordanting	Color obtained	*X*	*Y*	*Z*	*L**	*a**	*b**
Alum	Bright green	70.62	74.68	81.76	89.24	−0.34	−1.18
Ferrous sulphate	Dark green	5.45	5.84	5.28	29.02	−1.01	4.33
Stannous chloride	Purple	9.91	9.93	11.99	37.72	3.95	−3.68
Copper sulphate	Moss green	9.47	10.11	5.13	38.04	−0.91	20.61
Potassium dichromate	Green	28.81	29.95	18.05	61.61	1.68	23.43
Stannic chloride	Light purple	15.16	16.39	16.09	47.48	0.48	3.21

Table 3
Different pre-mordants, color obtained *X*, *Y*, *Z* and *L**, *a**, *b** values for dyed silk fabric with *Hibiscus mutabilis*

Pre-mordanting	Color obtained	*X*	*Y*	*Z*	*L**	*a**	*b**
Alum	Bright green	70.62	74.68	81.76	89.24	−0.34	−1.18
Ferrous sulphate	Dark green	5.45	5.84	5.28	29.02	−1.01	4.33
Stannous chloride	Purple	9.91	9.93	11.99	37.72	3.95	−3.68
Copper sulphate	Moss green	9.47	10.11	5.13	38.04	−0.91	20.61
Potassium dichromate	Green	28.81	29.95	18.05	61.61	1.68	23.43
Stannic chloride	Light purple	15.16	16.39	16.09	47.48	0.48	3.21

4. Results and discussion

4.1. Preparation and optimization of aqueous extract of *H. mutabilis*

The flowers of *H. mutabilis* were found to discharge color in hot water very easily. It is still better if the flowers were frozen after collection and then dipped in hot boiling water to get the maximum color in 30 min which shows deepening of hue color with temperature and time. Increasing the quantity of flowers from 2 g to 20 g per 100 ml water boiled for 60 min is accompanied with the increase in color strength and depth in color hue.

4.2. Optimization of mordants with *K*/*S* and color hue changes

Different mordants were used in 2–4% keeping in mind the toxicity factor of some mordants particularly copper and chromium. Varied hues of color were obtained from pre-mordanted cotton, silk fabrics and wool yarn with $FeSO_4$, $SnCl_2$, $CuSO_4$, $SnCl_4$, $K_2Cr_2O_7$ and alum when dyed by aqueous extract of *H. mutabilis*. As shown in Table 1, the different mordants not only cause difference in hue color and significant changes in *K*/*S* values but also changes in *L** values and brightness index values.

Table 4
Fastness properties for cotton fabric dyed with *Hibiscus mutabilis*

Pre-mordanting	Fastness properties					
	Washing (IS-687-79)	Light (IS-2454-85)	Rubbing (IS-766-88)		Perspiration (IS-971-83)	
			Dry	Wet	Alkaline	Acidic
Alum	4–4/5	IV	4–5	4–5	4/5	4/5
Copper sulphate	4–4/5	III	3–4	3	3–4	3–4
Ferrous sulphate	4–4/5	IV	3–4	3–4	3–4	3–4
Stannous chloride	4–4/5	III	4	3–4	3/4	4
Stannic chloride	4–5	IV	4	4	4	4
Potassium dichromate	4–4/5	IV	4	4	3/4	4

Table 5
Fastness properties for wool yarn dyed with *Hibiscus mutabilis*

Pre-mordanting	Fastness properties					
	Washing (IS-687-79)	Light (IS-2454-85)	Rubbing (IS-766-88)		Perspiration (IS-971-83)	
			Dry	Wet	Alkaline	Acidic
Alum	4–4/5	IV	4–5	4–5	4/5	4/5
Copper sulphate	4–4/5	III	3–4	3	3–4	3–4
Ferrous sulphate	4–4/5	IV	3–4	3–4	3–4	3–4
Stannous chloride	4–4/5	III	4	3–4	3/4	4
Stannic chloride	4–5	IV	4	4	4	4
Potassium dichromate	4–4/5	IV	4	4	3/4	4

Table 6
Fastness properties for silk fabric dyed with *Hibiscus mutabilis*

Pre-mordanting	Fastness properties					
	Washing (IS-687-79)	Light (IS-2454-85)	Rubbing (IS-766-88)		Perspiration (IS-971-83)	
			Dry	Wet	Alkaline	Acidic
Alum	4–4/5	IV	4–5	4–5	4/5	4/5
Copper sulphate	4–4/5	III	3–4	3	3–4	3–4
Ferrous sulphate	4–4/5	IV	3–4	3–4	3–4	3–4
Stannous chloride	4–4/5	III	4	3–4	3/4	4
Stannic chloride	4–5	IV	4	4	4	4
Potassium dichromate	4–4/5	IV	4	4	3/4	4

4.3. Fastness properties

It was observed that dyeing with *H. mutabilis* gave fair to good fastness properties in conventional dyeing. Table 1 shows L^*, a^* and b^* values and it can be seen that mordants which show higher value of L^* show lighter shades while lower L^* values signify deeper shades for cotton fabrics. Similarly, negative a^* and negative b^* represent green and blue, respectively. The colorfastness to washing was between 4 and 5 as shown in Tables 2 and 3 which are for silk and wool, respectively. We have compared the dyeing with conventional method. The fastness properties of dyed fabrics of cotton and silk are shown in Tables 4 and 5, while Table 6 shows fastness properties of wool yarn. Overall, it could be used for commercial purposes; the dyed cotton fabric, silk fabric and wool yarn attain acceptable range. The results clearly show that the aqueous dye of fresh flowers is better than dry flowers in terms of better dye uptake, reduced dyeing time and cost effectiveness.

5. Conclusion

Aqueous extract of *H. mutabilis*/Gulzuba flowers yields shades with good fastness properties. The dye has good scope in the commercial dyeing of cotton, silk and wool yarn. Preparation of dry powder is in progress so that this can be a cheap source of natural dye having good shelf life.

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