

**Delonix a source of Carotenoid
natural dye**

Use of delonix regia as dye

- The red flowers of Delonix regia have been evaluated for natural dyeing of silk using biomordant and enzymes for the first time, with a deliberate attempt to avoid metal mordanting in silk dyeing.
- This would make textile dyeing more ecofriendly. The present study was designed to evaluate the potential of this natural dye source for its dye content and to replace metal mordanting step by the use of enzyme or biomordant.
- The aqueous extract obtained from the dried red flowers was used for dyeing of silk fabrics. Good and bright reddish-brown hue color was observed when 30%, w/w with respect to the wt. of the fabric of delonix extract was used on the pretreated silk material. The silk fabric was treated with either enzyme or biomordant.

Dyed fabric

- Dyed fabric showed resistance to fading. Finally, all dyed specimens were tested for wash and light fastness properties, making delonix / gulmohar, a viable alternative to synthetic red dyes.
- Through desorption studies the order of reactivity of enzymes towards dye uptake in one step process was found to be Lipase> Diasterease>Protease--amylase = pyrus (biomordant). Similarly for two step the order of reactivity of enzymes was found to be Protease--amylase> Lipase> pyrus (biomordant) >Diasterease. Overall it can be concluded that in the case of enzymic and biomordant treatments, the two step process was better in terms of larger K/S values, Color coordinate values, fastness properties and dye adherence ability.

Flowers of delonix

Flower are large brilliant red-orange, occurring in numerous, huge terminal clusters at the ends of branches, each individual flower has 5 large, wide spreading petals (each 1 1/2 to 2 inches long), one petal streaked with white and yellow, flowering appears in early summer and continues for several months in Indian temperate climate. Thus delonix flower, though seasonal is abundantly available for dyeing purpose.

Purohit et al., have used different parts such as petal, calyx, petal and whole flowers of Delonix regia for cotton and silk yarn dyeing using metal mordant. This is the first report where delonix flower extract has been used in conjunction with a biomordant and enzymes for silk dyeing.

Chemical constituents of Delonix

- The red color in Delonix regia flower is most probably due to co-pigmentation between anthocyanins and other flavonoids , the color of the reddish-yellow flowers is mostly attributed to an increase in the isosalipurposide concentration, along with an increase in the background of the yellowish cytoplasmic carotenoids.
- A comparative study of the carotenoids present in various floral parts of Delonix regia has been made to gain information about the biogenesis and role of carotenoids in the flower. The qualitative and quantitative distribution of carotenoids was studied by chromatographic, spectrophotometric and other methods. The partition ratios, hitherto not reported, of a number of different carotenoids between different solvents are reported. The petals contain 29 carotenoids.
- The major pigments found were phytoene, phytofluene, β -carotene, γ -carotene, lycopene isomers, rubixanthin, lutein, zeaxanthin, and several epoxy carotenoids.

Chelation with Biomordant

Beside the anthocyanins of *Delonix regia*, other flavonoid present were identified, namely quercetin-3-rutinoside, quercetin-4'-glucoside, quercetin-3-glucoside, as shown in figure, 5-glucoside and chalcononaringenin-2'-glucoside. These pigments play an important role in dyeing of the fabric. Their chelation to biomordant or to enzyme would be a determining factor on their dye-ability.

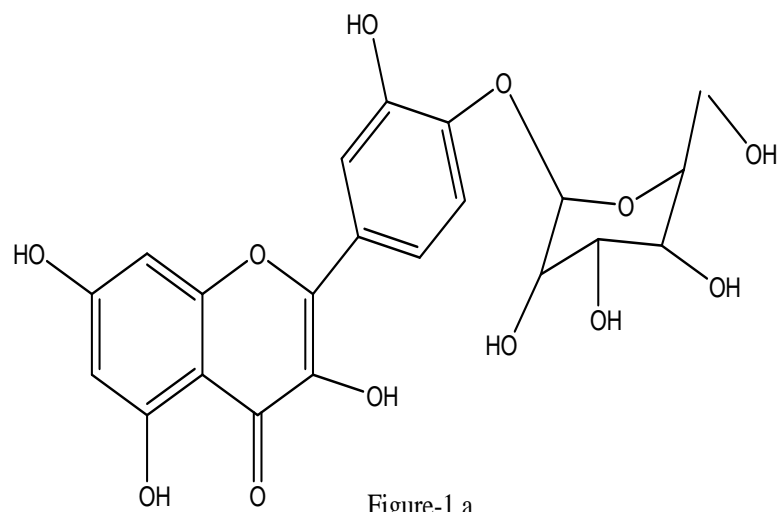


Figure-1 a

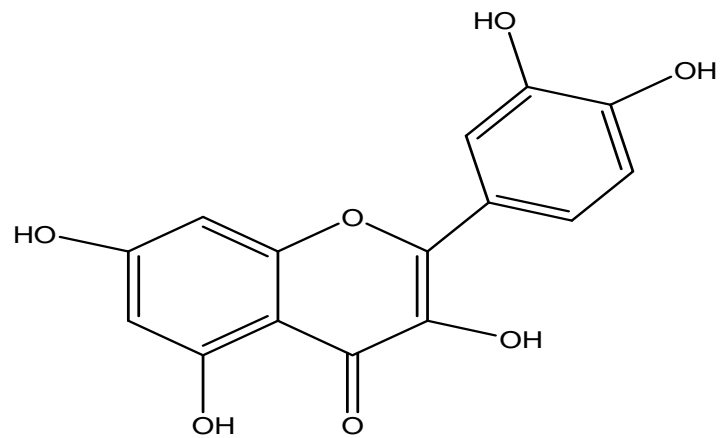


Figure-1b

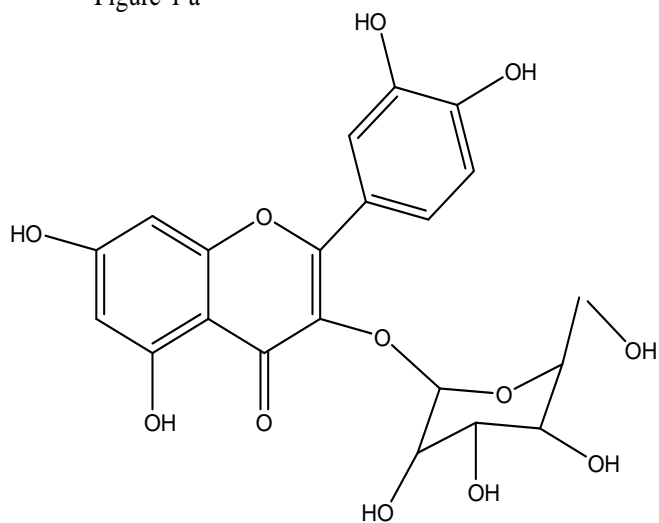


Figure-1c

Quercetin (b) and its different glucosides (a,c)

Pyrus having Copper

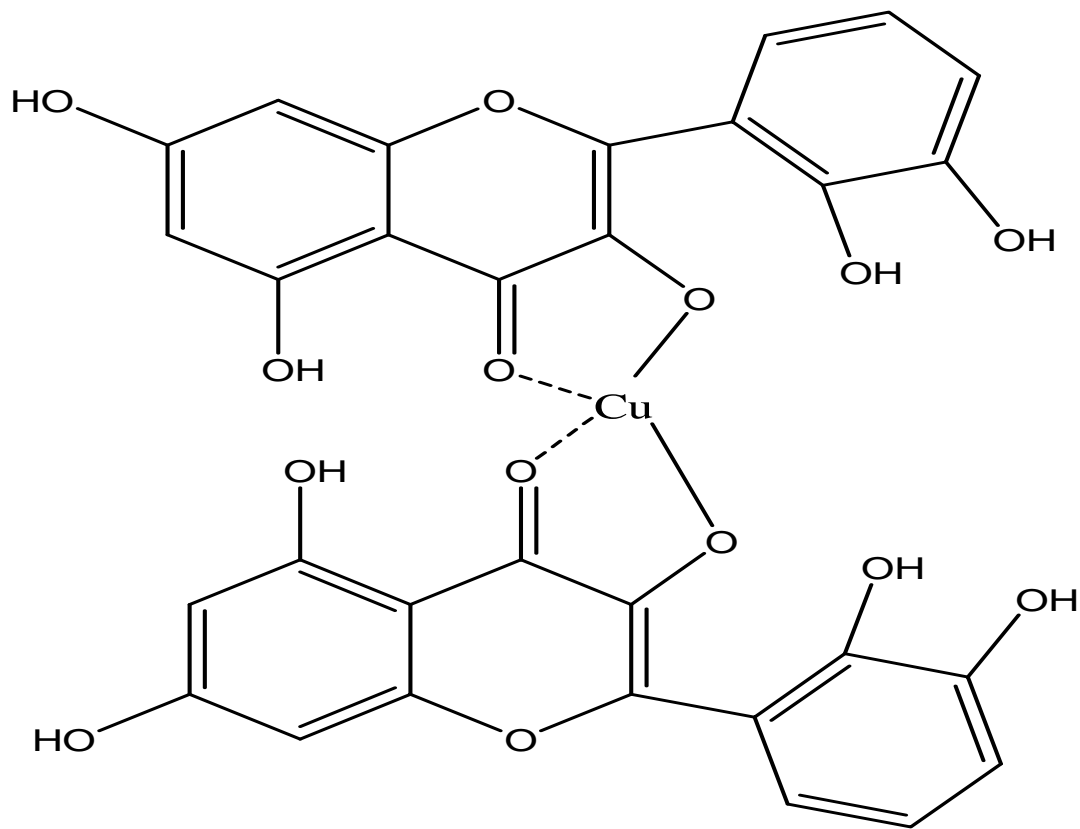
Pyrus pashia fruit (100gm in 1L deionized water) extract was prepared and analyzed by Atomic Absorption Spectroscopy and the analytical results show the presence of copper (Cu) in 10.66 mg/100gm.

It is present in some chelated form thus it might be helping the dye to adhere to the fabric similar to metal mordanting effect. The high Cu content suggested stronger and useful chelation to the colorant for better dye adherence.

Chelation with quercetin

The presence of the 4-oxo group in quercetin in conjunction with hydroxyl group also helps in chelation in flavonoids. Chelation of copper on the site between the 4-oxo group and C-5 OH group in flavonols and flavones has already been proposed.

The number of OH groups is also important, the higher the number, the higher their chelating ability is. Thus in the similar manner the copper in Pyrus helps in chelation of Cu(II) with the colorant comprising mostly of flavones/flavonols. Based on the above literature precedence the probable mode of chelation of copper in pyrus with quercetin has been proposed as shown in figure in the next slide. Chemical binding of the dye with biomordant has also been proposed analogous to metal-dye complex formation.



Probable mode of chelation of Cu of Pyrus with quercetin

Study of desorption of dye from dyed swatches

Extraction of the pigment of the dyed fabric in chloroform and measuring the absorbance of extract by spectrophotometer. The higher the dye desorbed the weaker is the dye adherence. The amount of dye desorbed by dyed silk fabrics derived by the two dyeing methods have been carried out. Substantial quantities of dye were desorbed from the samples of one step dyeing process which was an indication of poor dye adherence where as samples of two step dyeing process show very good dye adherence.

Desorption study

Desorption of dyed silk fabric showed the following results: In one step dyed fabrics diasterease treated fabric gave the best results where as in two step dyeing biomordant followed by protease-amylase showed the best results overall it can be concluded that in the case of desorption study of enzymic treatments and biomordant, the one step process desorbed larger quantity of dye, meaning thereby that dye adherence in one step process was poor for both enzymic and biomordant treated fabrics as compared to the two step dyeing process.

This was a clear cut indication that biomordant or enzyme first reacted with the silk fabric and then the treated fabric could adhere the dye well thereby showing good fastness properties.

Evaluation of Enzyme/Biomordant treated dyed fabrics for change in K/S and color strength:

The results of K/S and Color coordinate values have been shown for Delonix regia dyed silk fabrics treated with different enzymes such as Diastase, Lipase and Protease-Amylase and a biomordant Pyrus pashia by one step and two step dyeing process respectively.

The samples showed better dye uptake than control (untreated) as shown by increase in K/S value and color strength measured by the color measurement of dyed fabric using color scan machine.

Onestep vs two step results

It was found that in one step dyeing process lipase was the best option. The order of reactivity of enzymes in one step process observed was Lipase> Diasterease> Protease-amylase = pyrus (biomordant).

Similarly for two step dyeing process Protease and amylase combination enzymes was the best option. The order of reactivity of enzymes in one step process observed was observed to be Protease-amylase Lipase> pyrus (biomordant) >Diasterease.

Evaluation of metal mordant treated dyed fabrics for change in K/S and color strength:

Metal mordant treatments were also carried out with compounds such as Alum, Copper sulphate and Ferrous sulphate.

The purpose of using metal mordants was to compare the results with enzyme and biomordanted treated fabric swatches. It was found that results were comparable with that of enzyme and biomordant.

Results of metal mordanting

In the metal mordanting process we carried out one step and two and it was observed that the results of one step were far better than the two step method.

The mordant activity of the 3 mordants sequences was as follows: For one step dyeing process the order of reactivity was $\text{Cu} \rightarrow \text{Al} \rightarrow \text{Fe}$ and for two step dyeing process $\text{Fe} \rightarrow \text{Cu} \rightarrow \text{Al}$. This also explains the better reactivity of biomordant as it contains copper metal in pyrus fruit extract.

Biomordants

- Use of enzyme and biomordant were deliberate attempt to avoid metal mordanting in silk dyeing as it would make textile dyeing more ecofriendly. The order of reactivity of enzymes in one step process was found to be Lipase> Diasterease>Protease-Amylase = Pyrus (biomordant). Similarly for two step dyeing process the order of reactivity of enzymes in two step process observed was Protease-Amylase> Lipase> Pyrus (biomordant) >Diasterease. Protease and amylase combination enzyme was the best option.

Color strength effectivity

- The experiments showed that enzymatic and biomordant treatment can give good color strength to silk fabric using Delonix (Gulmohar) flower as a dye source and has good potential for commercial dyeing.
- Overall it can be concluded that in the case of enzymic treatment and biomordant the two step process was better in terms of larger K/S values, Color coordinate values and dye adherence. We have shown that the former two give comparable results with metal mordanted samples and thus were suited for industrial silk dyeing.

Role of enzyme

- Thus the role of enzyme in both the cases has been demonstrated to fix the dye molecules on the fibre surface which was not observed in the case of control sample (devoid of enzyme treatment) or in the case where denatured enzyme was used. The enzymes are adsorbed by virtue of various ionic and non ionic forces of attraction on to the silk fabric through hydrogen bonding, dipole-dipole interactions and electrostatic forces. The enzyme –dye complex thus formed on the surface of the dyed silk fabric acts as a barrier for not letting the dye get washed off.

Enzyme-complex

The probable reason for the superiority of two step dyeing process over the one step process could be due to the fact that sequential treatment to the silk fabric may be resulting in formation of the large molecular size and low water solubility complex on the surface of the silk fabric. Good light fastness in the case of two step process could be attributed to the antioxidant property of the biomordant Pyrus and similarly the results obtained from protease-amylase enzymic treatment are found to follow the same trend