

Dyeability of Cellulose Fibers Using Dyestuff from African Rosewood (*Pterocarpus erinaceus*)

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ABSTRACT: Methanol extracted from the “heart wood” of the plant *Pterocarpus erinaceus* (African rosewood) gave a brick red dyestuff. Chromatographic separation of the dye produced a single homogenous component with an *R_f* value of 0.78, a yield of about 17.3% and a melting point of 86°C. IR spectrum of the purified dye showed the presence of an aromatic C=C double bond band at 1620–1470 cm⁻¹ and NH₂ absorption characteristic of an aromatic amine N—H stretch at 3590–3400 cm⁻¹, while para-disubstitution on aromatic nucleus was observed at 850–840 cm⁻¹. A wavelength of maximum absorbance, λ_{max}, of 500 nm was recorded on a UV/visible scan for the solvent soluble dye. The dye, which was substantive to cotton, was applied quantitatively to it and reed fibers by exhaust dyeing technique from locally distilled alcohol. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 746–751, 2000

Key words: African rosewood; resin; tannin 0; industrialist

INTRODUCTION

The plant African rosewood is a deciduous hardwood with a tall, narrow open crown bearing winged fruit that is descriptive of its modified pod. Slashes or incisions on the trunk of the tree produce a copious red gummy exudate that dries to a blood-red resin.

The red heartwood is used to prepare a red dye that is quite substantive to cotton. The dye, apart from its substantivity to cellulosic fibers, is also widely used for medicinal purposes. For instance, the red gum obtained from most *Pterocarpus* trees was reportedly used as astringent in treating diarrhea and dysentery, and its use as a color additive in some wine brewing has equally been reported.¹

The dyeing of cotton fabric in a dyebath prepared using a natural dyestuff of the type ob-

tained from the *Pterocarpus* species is an old technology, with a history dating as far back as 5000 BC and is certainly not practiced now on a large industrial scale because of the availability of cheaper and technically more efficient synthetic dyestuff.² However, dyestuffs in this category are still used for handicrafts by cottage industrialists, who still process cellulosic fibers on a small scale for household items such as floor carpets (made from plant reed fibers) and cotton textile materials.³

The work described in this article is part of a systematic attempt to discover suitable indigenous dyes and pigments that can be developed for use on woven cellulosic fibrous constructions, mostly floor carpets (foot and sleeping mats) and fabrics designed for wearing apparel, with the objective of promoting local sourcing of dyes and pigments for use in cottage industries. The comparative fastness ratings of this and related dyes on these fibrous constructions are assessed in the second part of this study.

EXPERIMENTAL

Extraction and Purification of the Dye

The *Pterocarpus* [heartwood] used was purchased off the market. It was first dried in the oven at 110°C for 6 h before being pulverized to aid solvent extraction. About 20.8 gm of the pulverized sample was first washed with n-hexane in a soxhlet extractor prior to extraction of the pigment. This is to remove oil where available. Subsequently, the sample was extracted using methanol for 6 h. The solvent was later recovered by distillation while the crude dye was separated for recrystallization following drying at 105°C for 3 h. Recrystallization was carried out in chloroform : ethylacetate (3 : 2 v/v).

Chromatographic Separation

As a means of further purification, the dye extract was fractionated by column chromatography over alumina in a glass column. The sample was dissolved in a minimal amount of methanol and introduced on top of the column. The compounds were subsequently eluted using solvents of varying polarities as follows:

- Hexane, 200 mL;
- Hexane : benzene (80 : 20 v/v), 200 mL;
- Benzene, 200 mL;
- Benzene : chloroform (75 : 25 v/v), 200 mL;
- Benzene : ethanol (80 : 20 v/v), 200 mL;
- Benzene : ethanol (20 : 80 v/v), 200 mL;
- Ethanol 200 mL

The fractions collected were spotted on T.l.c. in chloroform : acetone (90 : 10 v/v) for 10 min, and spots were detected with sulfuric–nitric acid reagents and bromocresol green.

Spectroscopic Studies

Both the IR and UV–visible spectra of the dyestuff were scanned. The IR was run on a Pye Unicam SP3-300 IR machine, while the UV–visible was carried out using a Pye Unicam SP8-400 spectrophotometer.

Preparations of Fibers for Dyeing

Two types of cellulosic fibrous constructions were used for dyeing: (1) pure (100%) cotton fabric

scoured and bleached pure white (supplied by Nigerian Chemical and Textile Co., Lagos) was used both as a control and also was pretreated in 5% ferric alum salt as a mordant; (2) reed fibers obtained from the plant *Thaumatococcus danielli* commonly used for carpet weaving were also processed for dyeing in a manner similar to the cotton fabric.

Determination of Density of the Fibers

The Davenport two-column density-measuring apparatus was used to determine the densities of the fibers. The density gradient column was filled with a mixture of CCl₄–n-heptane to give a working range of 1.45–1.30 g/cm³ at 23.0 ± 0.1°C. The column was calibrated with glass floats of known densities. Then the fiber samples were dropped in the column and allowed to equilibrate for 24 h, after which their respective positions were read and their densities obtained from the calibration standard by interpolation.

Dyeing of Fibers

Two separate dye baths were prepared, each containing the same amount (1 g) of the pure dyestuff dispersed in 1000 cm³ of locally distilled alcohol contained in a 2-L culture flask equipped with thermometer and stirrer. One bath was used for the dyeing of the cotton fabric, both control and mordanted, while the other was used for the reed fiber. Then 2.0 g of each specimen (cotton or plant fiber) was introduced into the dyebath at the temperature of dyeing *T_d* 80°C, and dyeing was carried out continuously for periods ranging from 15 min until equilibrium (a point of saturation of the fibers with dyestuff) was established, usually after about 15 h of continuous dyeing at the boil point. A high, uniform stirring speed was maintained throughout the period of dyeing to ensure that the dyestuff was in a dispersed state. After each dyeing the specimen was removed and put into cold running water to arrest further dyeing, washed in distilled water, and dried in a vacuum oven set at 60°C/15 mm Hg.

Quantitative Determination of Fixed Dyes on Fibers

Dye uptake by each dyed sample was determined by extracting 10 mg of each dried sample using 10 mL of Spectrosol-quality dichloro methane, which was found suitable for stripping the dye by heat-

Table I Physicochemical Parameters Obtained for the Dye Obtained from *P. erinaceus* (African Rosewood)

Parameter Examined	Result Obtained
Appearance	Solid crystals; brick red in color
Yield	Ca. 17.3%
Melting point	86°C
Solubility	<i>Solvents</i> (good) methanol, ethanol, propanol, 5% NaOH <i>Partial</i> benzene, chloroform

ing under reflux for 30 min. The extract was then made up accurately to 10 mL and its optical density measured on the Pye Unicam SP8-400 UV-visible spectrophotometer at the wavelength of maximum absorption (500 nm) determined for the dye (Fig. 2).

Dye solutions of varying concentrations had earlier been prepared and their absorbance determined at the same wavelength of 500 nm, and the validity of the Beer-Lambert law had been established by a linear correlation between the dye concentration (in mg/L) and the optical density. Consequently, the amount of dye uptake was determined using eq. (1) as follows:⁴

$$\% \text{ Dye uptake (mg/g)} = \frac{\text{optical density} \times \text{volume of extract} \times \text{dilution}}{\text{extinction coeff} \times \text{wt. of dyed sample} \times 1000} \times 100\% \quad (1)$$

RESULTS AND DISCUSSION

Table I lists the physicochemical properties obtained for the pure dye extract from *P. erinaceus*.

Column and T.I.c. Results

The various fractions collected from the column chromatography following purification of the dye were spotted on [T.I.c.] A single *R_f* value of 0.78 was obtained. This is an indication of the presence of a single component rather than a mixture in the dyestuff.

UV-Visible Results

Two spectra were obtained, one for the crude dye (Fig. 1) and the other for the purified dye (Fig. 2).

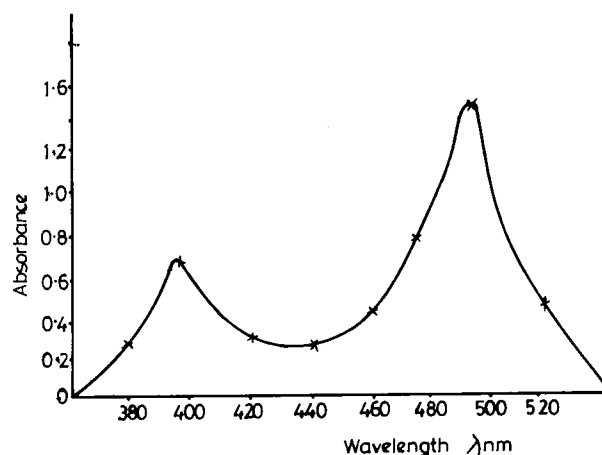


Figure 1 Electronic absorption spectrum for the crude dye obtained from *Pterocarpus erinaceus*.

The crude dye gave two absorption maxima, at 400 nm and at 500 nm, respectively. The intensity of the former was considerably lower than that of the latter, indicating a possible yellow contaminant (since the wavelength of 400 nm corresponds to the transmission of a yellow color). However, following the recrystallization of the dyestuff, it was observed that the absorption maximum at 400 nm disappeared, leaving a single component dye with an absorption maximum at 500 nm.

Since this absorption falls within the visible region of the electromagnetic spectrum, it shows that the extract contains a strong color-imparting chromophore and that the dye itself, being a

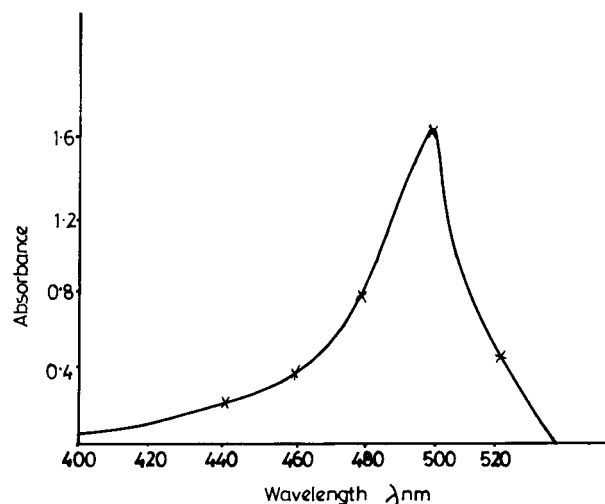


Figure 2 Electronic absorption spectrum for the pure dye obtained from *Pterocarpus erinaceus*.

Table II Infrared Absorption Frequencies for the Pure Dye Obtained from *P. erinaceus*

Absorption Frequency (cm^{-1})	Mode of Vibration	Interpretation
3590–3400	N—H structure	Broad-banded OH^- stretch in hydroxyl group of phenolic compounds. NH_2 in aromatic amines.
1620–1470	C=C stretching	Aromatic ring
1210–1170	C—N stretching	Aromatic ring
850–840	C—H out of plane deformation	Aromatic para-disubstitution

monocomponent material, is also made up of one hue, which in this case is predominantly red. The hue (or color) transmitted by a dyestuff or pigment is determined by the predominant wavelength of its absorption of light energy. The transmission of a red color by the dyestuff in this study shows that a spectral color corresponding to turquoise has been absorbed, leaving a color complementary to red to be transmitted.⁵

A sharp absorption peak recorded for the pure dye (Fig. 2) indicated high-quality color transmission characteristic of a single color component as against a broad absorption spectrum, which spreads fairly evenly over several contributing colors in a typical color mixture.⁶

Infrared Results

The prominent IR absorption peaks observed for the pure dye are shown in Table II.

The presence of both a hydroxyl group ($-\text{OH}$), due to the aromatic phenolic compound, and of NH_2 in aromatic amine is indicated. Absorptions at $1620\text{--}1470\text{ cm}^{-1}$ and $1210\text{--}1170\text{ cm}^{-1}$ are due to the presence of C=C bond in an aromatic ring as well as C—N, while absorption at $850\text{--}840\text{ cm}^{-1}$ strongly indicates the presence of para-disubstitution on the benzene ring.

Although it is not the objective of this study to characterize fully the structure of the dyestuff obtained, it may be suggested that the color-bearing body of the dye is a simple conjugated aromatic compound with a fused C=C chromophore of the ethylene group. The presence of NH_2 and $-\text{OH}$ groups as auxochromes to the coloring molecule may also be deduced from the several IR absorptions characteristic of the $-\text{OH}$ and N—H bonds earlier discussed.

Dyeing Results

The dyeing of cellulosic fibers (both cotton and plant fibers) on a handicraft scale using dyestuffs from plant sources is a flourishing industry among women in many developing countries. For such cottage industrialists, the development of fast, easily affordable, and substantive dyestuffs is a priority program of their respective governments. The dyestuff from African rosewood has been reported to be substantive to cotton.¹

The results obtained for the dyeing of cotton fabric, both mordanted and control, are shown in Figure 3. Also shown are the parallel results for

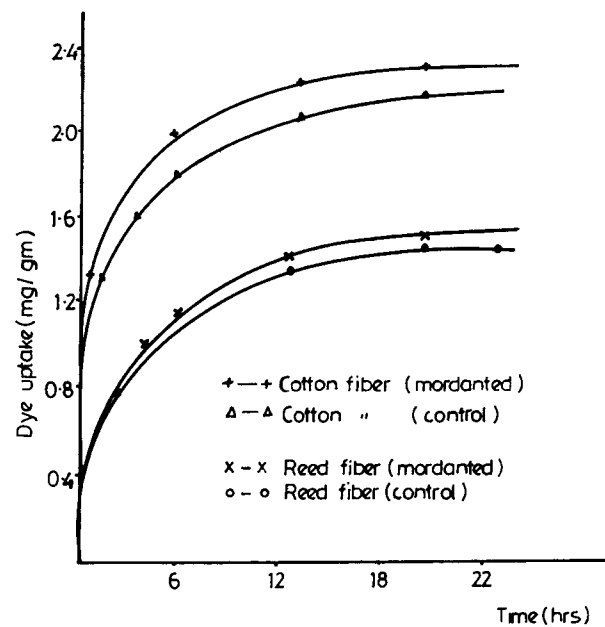


Figure 3 Dye uptake versus time of dyeing for cotton and reed fibers dyed using dye extract from *Pterocarpus erinaceus*.

Table III Densities, Crystallinities, and Equilibrium Dye Uptakes for Cotton and Reed Fibers Dyed Using Dyestuff from African Rosewood at 80°C

Fiber's Detail	Density (g/cm ³)	Crystallinity (%)	Equilibrium Dye Uptake (mg/gm)
Cotton fabric control	1.382	42.3 (57.7) ^a	2.20
Mordanted	1.382	42.3 (57.7)	2.38
Reed fiber control	1.400	56.4 (43.6)	1.42
Mordanted	1.400	56.4 (43.6)	1.50

^a Assumed percentage amorphous content in parentheses.

the dyeing of the reed fibers used in the manufacture of carpets.

From the results shown, the following observations can be made: (1) Dyeing proceeds faster with the cotton fabric than with the reed fibers given both a higher rate of dyeing and equilibrium dye uptake; and (2) The presence of the mordant increases both the rate of dyeing and the equilibrium dye-uptake for the two fibers still.

Both the rate of dyeing and the equilibrium dye uptake by a fiber are determined by the dye diffusion characteristic of the polymer structure being dyed. Several factors have been identified to influence this dye diffusion characteristics by previous workers and have been a subject of extensive study.⁷ Some of these factors include: the presence of functional groups within the fibers being dyed, pH, ionic strength, temperature and degree of swelling of the fibers, moisture absorptivity, and the prehistory of the fibers. Since the fibers being dyed are cellulose and the conditions of dyeing employed are uniform, most factors considered are assumed constant, with a single measurable parameter (factor) exerting an influence on the dyeing behavior of the fibers; what has been taken into consideration, however, is the degree of compactness (or crystallinity) of both fibers. The more compact-crystalline a polymer is, the less accessible it becomes to diffusing molecules.⁸ The values obtained for the densities of the various fibers are about 1.382 g/cm³ for the cotton fabric and about 1.400 g/cm³ for the reed fiber. These values correspond to crystallinity values of 42.3% and 56.4%, respectively (Table III). If the fibers are assumed to be composed of crystalline and amorphous phases only, then the corresponding amorphous content for the cotton will be 57.7% while that of reed plant will be 43.6%. These values are shown in parentheses in Table

III. Since the region that is accessible to dyes within the polymer is the amorphous phase only, with a higher amorphous volume available for dye uptake in the cotton fiber, both the rate of dyeing and equilibrium dye uptake for cotton fabric will be expected to be significantly higher than that of the reed fiber that has lower amorphous volume, as the case is in this study.

The Role of Ferric Alum Mordant (NH₄Fe(SO₄)₂ · 12H₂O)

Mordants are usually salts of inorganic elements, such as iron and aluminum, or synthetics such as ketanol 0 and tanninol BM, which on treatment with natural fibers such as cotton or jute are capable of enhancing dye uptake. This is usually achieved by forming complexes with the dyestuff that are capable of opening up the fiber structure and allowing dye diffusion into the fiber. The role of the 5% alum mordant used in the dye uptake was assessed by comparing the equilibrium dye uptake of the mordanted fibers with the control (without mordant). The data presented in Table III shows an increase in the equilibrium dye uptake, from 1.42 mg/gm for the unmordanted reed fiber to 1.50 mg/gm for the one treated with mordant, a marginal increase of 5.6% in the dye uptake over the control sample. A similar result was obtained with the cotton fiber, where the equilibrium dye uptake increased from 2.20 mg/gm to 2.38 mg/gm, representing an increase of 8.18% over the control fiber.

With an increase of 54.9% over the equilibrium dye uptake of the reed fiber, the cotton fabric can be considered sufficiently substantive to the dye from African rosewood, and given sufficient fastness properties, it can be recommended for cottage industrial applications.

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