

Anthraquinone Glycoside from Stem Bark of *Cassia reingera* and Use of Aqueous Bark Extracts as An Eco-friendly Natural Dye on Wool

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From the bark of *Cassia reingera* 1,5,6-trihydroxy-3-methyl anthraquinone-8-O-L-glycoside has been isolated and its structure elucidated with the help of chemical studies and spectral data. The dyeing property of crude anthraquinone has been studied to develop variety of shades on wool by dyeing with different mordants.

Key Words: Anthraquinone glycosides, Pre-mordanting, *Cassia reingera*.

INTRODUCTION

The increasing awareness of environmental pollution associated with synthetic processing and use of synthetic dyes has lead to a worldwide interest in dyeing textiles with flora and fauna. Natural dyes procured from natural wealth like plants, minerals and insects are fairly non-polluting. These dyes are gaining importance in recent years because of carcinogenic nature of synthetic dyes. The non-toxic, biodegradable properties of natural dyes are making them exceedingly popular. These dyes are useful for human health.

Anthraquinones¹⁻³ is the main source of natural dyes. The present paper deals with the isolation and characterization of anthraquinone from stem bark and use of crude dye extract as natural dye⁴ on wool.

EXPERIMENTAL

The stem-bark of *Cassia reingera* was collected from natural source and identified by taxonomist. The bark was dried under shade and pulverized in wiley mill to powder form. The air-dried and crushed stem-bark (3 kg) of *Cassia reingera* was repeatedly extracted with boiling ethanol in Soxhlet extractor and concentrated under reduced pressure in a rotatory evaporator till the weight of concentrated extract became 5 g. It was then poured into an excess of ice-cold water to give water-soluble and water insoluble portions. The water-soluble portion was extracted successively with different solvents. The ethyl acetate extract on concentration gave reddish

brown pigment. Thin layer chromatography by silica gel plate using solvent system, chloroform:ethyl acetate:methanol (4:4:12, v/v) gave compound **1** (2 g). This compound was found to be glycoside by positive Molisch's test and did not reduce Fehling solution.

Use of aqueous bark extracts: Bark was dried under shade and pulverized in Wiley Mill to powder form. Wool was purchased from a carpet house in Agra. Chemicals such as potassium dichromate (chrome), potassium aluminium sulphate (alum), strontium nitrate, nickel sulphate, barium chloride, copper sulphate and chromium nitrate and manganese acetate were used as mordants.

The wool were soaked⁵ in tap water for 0.5 h. The optical density was measured by Elico SL-159 spectrophotometer integrated with Zenith PC at 380 nm. The dye liquor was prepared by taking different amounts (2, 4, 6, 8 and 10 g) of dry bark powder in 100 mL of water. These were extracted for 1 h and filtered. Two mL of aliquot was taken as a sample and diluted to 5 times to record optical density. The wool samples weighing 1 g each were dyed in the dye solution for 1 h at 100 °C. The optical density of left over dye solution was recorded (Table-1).

Mordanting: The three methods of mordanting *i.e.* pre-mordanting, simultaneous and post-mordanting were tried for each mordant. It was observed on the basis of visual evaluation that pre-mordanting method improves the intensity of colour evenness and overall appearance of the sample. Thus this method was selected for further experiments.

In premordanting method⁶, mordanting was carried out prior to dyeing. The required amount of mordant was dissolved in 10 mL boiling water. The solution was transferred to a beaker containing 90 mL of warm water. The soaked samples were added to the solution and temperature was raised at 100 °C. The solution was stirred occasionally to bring an even distribution of mordant over the wool fiber. Mordanting was continued at this temperature for 1 h, then the samples were allowed to cool in the mordant solution and dried under shade. The samples mordanted with chrome, ferrous sulphate, copper sulphate and stannous chloride were dried immediately after mordanting, whereas the samples mordanted with alum were left overnight to give best shades. In case of mordanting with chrome the dye bath was properly covered because chrome is very sensitive to light.

In order to find out the optimum concentration of the various metallic mordants, different concentration of each mordant, namely 2 % conc. of alum, barium chloride, manganese acetate, 1 % of potassium dichromate, strontium nitrate, nickel sulphate, copper sulphate and chromium nitrate and 1.5 % of ferrous sulphate were used to dye the wool samples.

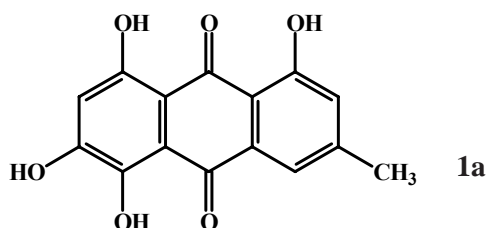
Colourfastness⁷ of dyed sample towards light was measured by Fed = 0 = meter while launder = 0 = meter was used to check the colourfastness to washing and staining.

RESULTS AND DISCUSSION

Compound 1: Crystallized from EtOAc-petrol (3:1), M^+ 448, m.p. 190 °C (Found: C, 56.25; H, 4.40. Calcd. for $C_{21}H_{20}O_{11}$: C, 56.25; H, 4.46 %); UV; 235, 255, 300 and 470 nm; IR: 3420, 3300, 2920, 1640, 1550, 1475, 1450, 1375, 1360, 1300, 1230, 1220, 1100, 1030, 990, 890, 870, 835 and 770 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$): δ 3.85 (6H, sugar protons), 5.02 (H-1'-glucosyl), 2.26 (3H, s, Me), 7.00 (s, 1H, C₇-H), 7.25 (br, 1H, C₂-H), 7.75 (br, 1H, C₄-H). This compound was characterized as 1,5,6-trihydroxy-3-methyl anthraquinone-8-O-L-glycoside.

Acid hydrolysis of compound 1: Compound 1 was refluxed in MeOH with 7 % H_2SO_4 at 65 °C for 6 h on a water-bath to obtain aglycon. The aglycon thus obtained was crystallized from C_6H_6 -EtOAc (4:1), m.p. 220 °C (Found: C, 62.80; H, 3.54. Calcd. for $C_{15}H_{10}O_6$: C, 62.90, H, 3.49 %). It responded to positive colour test for an anthraquinone⁸⁻¹⁰ (appearance of red colour with methanolic sodium hydroxide as well as with methanolic magnesium acetate). UV: 235, 255, 310, 475 nm; IR: 3450, 3272, 2920, 1610, 1545, 1475, 1450, 1375, 1360, 1230, 1100, 1030 nm; 1H NMR (250 MHz, $CDCl_3$): 2.26 (3H, s, Me), 7.00 (s, 1H, C₇-H), 7.20 (br, 1H, C₁-H), 7.80 (br, 1H, C₄-H), Mass: m/z : 286 (M)⁺, 268, 258, 240, 230, 183, 110, 108. Ethanol and water extracts of this pigment were taken to obtain variety of shades⁹ on wool. These extracts were used to dye the wool samples on dye bath at 70-80 °C for 1 h. Many mordants such as alum, pot. dichromate, tartaric acid, were used for dyeing to obtain number of colourful shades on wool. This aglycone **1a** was characterized as 1,5,6,8-tetrahydroxy-3-methyl-anthraquinone.

Wool was selected for dyeing^{9,11,12} because it is a protein fiber in which both acidic and basic groups are present. Hence its dye affinity is greater than that of cotton fiber. Out of three methods of mordanting namely pre-mordanting (A), simultaneous (B) and post mordanting (C), method (A) was considered to be the best with all mordants mentioned in Table-2.



It is evident that percentage of absorption of dye increases with the increase in dye concentration and it reaches maximum when 6 g (Table-1) of dye material was used. Similarly 1.5 h of extraction time give optimum optical density (Table-3) while there was not so significance increase in the optical density even after boiling for 2 h. Among all the mordants used in the study, copper sulphate gave most appealing shades on wool^{13,14}.

TABLE-1
PER CENT ABSORPTION FOR DIFFERENT CONCENTRATION OF
Cassia reingera BARK POWDER

Wavelength (mm)	Concentration of bark powder 1 g/100 mL water	O.D. before dyeing	O.D. after dyeing	Absorption (%)
380	2	0.06	0.05	16.60
380	4	0.18	0.14	22.22
380	6	0.23	0.15	38.88
380	8	0.50	0.35	30.00
380	10	0.92	0.72	21.73

TABLE-2
PER CENT ABSORPTION FOR DIFFERENT MORDANTING
METHODS WITH *Cassia reingera* STEM BARK
Mordanting method-premordanting; Weight of wool sample-2 g

Wavelength (nm)	Mordants	Concentration of mordants	Absorption (%)
380	Alum	2.0	47.50
380	Manganese acetate	2.0	50.20
380	Ferrous sulphate	1.5	42.22
380	Potassium dichromate	1.0	64.22
380	Strontium nitrate	1.0	60.21
380	Nickel sulphate	1.0	47.08
380	Copper sulphate	1.0	50.04
380	Barium chloride	2.0	43.05
380	Chromium nitrate	1.0	46.89

TABLE-3
OPTICAL DENSITY AT DIFFERENT PERIODS OF
BOILING OF *Cassia reingera* STEM BARK

Wavelength (nm)	Time of boiling (h)	Optical density
380	0.5	0.150
380	1.0	0.160
380	1.5	0.185
380	2.0	0.186

TABLE-4
RATING FOR COLOUR FASTNESS OF SAMPLES DYED WITH *Cassia reingera*
WATER EXTRACT AND TREATED WITH DIFFERENT MORDANTS

Treatment	Rating for colour fastness	Rating for light fastness
Samples without mordant	Good	Fairly good
Manganese acetate	Fairly good	Good
Ferrous sulphate	Fair	Poor and v-poor
Potassium dichromate	Fairly good	Good
Strontium nitrate	Good	Very good
Nickel sulphate	Good	Very good
Copper sulphate	Fair	Fairly good
Barium chloride	Poor and v-poor	Fair

Out of large number of samples generated during present study, some samples were selected for light and wash fastness. All the samples dyed by pre-mordanting dyeing method, exhibited fair good to good fastness, while few samples showed poor light and wash fastness (Table-4). From the above study it can be concluded that a unique bands of colours can be obtained from natural dyes by using chemical mordants. Their light and wash fastness is only fair to good in the majority of cases.

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