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NOTE

Isolation and characterization of anthraquinones from the stem bark of *Cassia* species

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Abstract : 1,8-Dihydroxy-6-methoxy-3-methyl anthraquinone from stem bark of *Cassia fistula* and 1,8-dihydroxy-3-methyl anthraquinone and bianthraquinone cassiamin from stem bark of *Cassia siamea* have been isolated and their structures were elucidated by spectral studies. Ethanolic bark extracts of both the plants were used as natural dyes on wool.

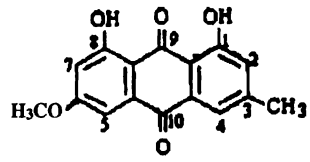
Keywords : Anthraquinone, plant pigment.

Cassia (Family : Leguminosae; subfamily : Caesalpiniaceae) is a large dominating tropical genus with about 580 species of herbs, shrubs and trees. Many of them are of medicinal importance and a few are sources of tanning material of economic value. Species of *Cassia* are rich source of flavonoids, anthraquinones and polysaccharides. The barks of these two plants are major source of natural dyes. These dyes are gaining importance in recent years because of carcinogenic nature of synthetic dyes.

The present paper deals with the isolation and characterization of dye yielding plant pigment anthraquinones from the bark of *Cassia fistula* and *Cassia siamea* and use of bark extracts as a natural dye. This experiment was carried out to revive old art of dyeing with natural dye. Barks of both the plants were collected from the natural sources and identified by taxonomist. The barks were dried under shade and pulverized in wiley mill.

Results and discussion

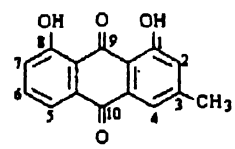
(a) Study on bark of Cassia fistula[1] : The pigment (m.p. 270°) was brown in colour, $C_{16}H_{12}O_5$, UV (EtOH) 410 nm; IR (KBr/cm^{-1}) 2940 (phenolic OH), 1660 (non-chelated C=O) and 1635 cm^{-1} (chelated C=O); ^{1}H NMR spectrum of compound **1** showed signals for one C-methyl at δ 2.42 (3H, s, C-3), one methoxy group at δ 3.91 (3H, s,), two phenolic peri-hydroxyl groups at δ 12.08 and 12.28 (each broad singlet exchangeable with D_2O, 1H, 2 × OH, C-8 and C-1) and four aromatic protons at 6.66, 7.34 (1H, s, d, *J* 2 Hz, H-2 and H-4) and 7,05, 7.59 (each 1H, d, *J* 2 Hz, H-7 and H-5) was characterized as 1,8-dihydroxy-6-methoxy-3-methyl anthraquinone[2] (**1**).



(1)

(b) Study on Cassia siamea stem bark : Two pigments[3] namely, chrysophanol (**2**) and cassiamin (**3**) were isolated by thin layer chromatography of concentrated bark extract.

Compound **2** : Crystallized from chloroform : methanol (1 : 1) as yellow needles, m.p. 195°, $C_{15}H_{10}O_4$ (M^+ 254), R_f value 0.28 (chloroform : benzene : methanol 16 : 3 : 1, v/v); UV (EtOH) 257, 277, 287, 429 nm; IR (KBr/cm^{-1}) 3400, 1670, 1620 cm^{-1}; NMR ($CDCl_3$) one methyl group at δ 2.42 (3H, s, C-3), two chelated phenolic hydroxyl group at δ 12.10 and 11.99 (2 × OH, C-8 and C-1), 5 aromatic protons at δ 7.03 (1H, s, H-2) and 7.10–8.10 (4H, m, H-4, H-5, H-6, H-7). It was characterized as 1,8-dihydroxy-3-methyl anthraquinone[4].



(2)

Compound **3** : Crystallized from tetrahydrofuran as yellow orange prism, m.p. 356–357° (decomp.), R_f value 0.42

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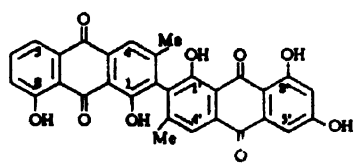
(chloroform : benzene : methanol 16 : 3 : 1, v/v); UV (EtOH) 228, 259, 288 and 444 nm, resembles those of 1,8-dihydroxy anthraquinones such as, chrysophanol (UV (EtOH) 257, 277, 287 and 429 nm) and emodin (UV (EtOH) 222, 261, 289, 437 nm).

The IR carbonyl absorption of the compound at 1670 cm^{-1} indicated the presence of CO group. The IR absorption band in the region of 1620 cm^{-1} was assigned to olefinic/aromatic linkage vibration, singly chelated anthraquinone carbonyl absorb in the region 1631–1637 cm^{-1}, in which compound has no absorption maximum, indicating that the α-hydroxyl of neither anthraquinone moiety were in 1,4 or 1,5 relationship.

The ^1H NMR ($CDCl_3$) spectrum showed signals for two methyl groups at δ 2.40 (s), δ 2.42 (6H, s, C-3, C-3′), seven aromatic protons at 7.93 (1H, s, H-4), 7.66 (3H, m, H-5, H-6, H-7), 7.84 (2H, s, H-4′, H-5′), 7.93 (1H, s, H-7′). This was further supported by closed resemblance of electronic spectrum of bianthraquinone-cassiamin[5] to the spectra of chrysophanol and emodin.



(3)

(c) Ethanolic bark extracts use as natural[6] dye on wool : In this investigation optimum concentration of dye material, extraction time, dyeing time were observed from dye extracted from the bark of both the plants on wool. Wool was subjected for dyeing process because it is a protein fibre in which both acidic and basic groups are present. Hence its dye affinity is greater than that of cotton fibres. It is evident (vide Tables 1 and 2) that percentage of absorption of dye increases with increase in dye concentration and it reaches maximum when 0.75 g/100 ml water, ethanolic extrat solutions were used.

Table 1. Percentage absorption for different concentrations of ethanolic bark extracts of *Cassia fistula*

Sl. no.	Wave length (nm)	Concentrated ethanolic extracts in g/100 ml water	O.D before dyeing	O.D. after dyeing	Percent absorption
1.	380	0.25	0.08	0.07	12.50
2.	380	0.50	0.19	0.15	21.05
3.	380	0.75	0.25	0.17	32.00
4.	380	1.00	0.50	0.35	30.00

Table. 2. Percentage absorption for different concentrations of ethanolic bark extracts of *Cassia siamea*

Sl. no.	Wave length (nm)	Concentrated ethanolic extracts in g/100 ml water	O.D. before dyeing	O.D. after dyeing	Percent absorption
1.	380	0.25	0.06	0.04	16.60
2.	380	0.50	0.17	0.14	17.65
3.	380	0.75	0.22	0.12	45.45
4.	380	1.00	0.50	0.36	28.00

Experimental

(a) Bark of Cassia fistula[7] : The air-dried, crushed and defatted stem bark (1 kg) was repeatedly extracted with boiling ethanol, concentrated under reduced pressure in a rotavapour and poured into an excess of ice cold water to get water insoluble and water soluble portions. The water soluble portion was successively extracted with ether and ethyl acetate. The ether extract had no colour residue while ethyl acetate extract on concentration afforded a brown coloured pigment. The brown pigment was subjected to thin layer chromatography by silica gel coated glass plate using chloroform : ethyl acetate : methanol (4 : 6 : 10, v/v) solvent system. It was found to be homogeneous. It responded positively with methanolic magnesium acetate and sodium hydroxide for an anthraquinone. This anthraquinone was identified on the basis of colour reactions, spectral data, and co-TLC with the natural product isolated from the other species of *Cassia* plants[8].

(b) Bark of Cassia siamea : The air-dried and powdered bark (500 g) was successively extracted in a soxhlet extractor with hexane, chloroform and ethanol. The total percentage was found to be 18.36%. The ethanolic extract (13.71%) was concentrated under reduced pressure. The concentrated mass of ethanolic fraction on chromatography over silica gel column using benzene : chloroform (4 : 6) as eluent gave a yellow coloured compound **1** (300 mg). Further elution with chloroform : methanol (6 : 4) afforded an orange yellow compound **2** (700 mg). Compound **2** and compound **3** gave red colour with methanol magnesium acetate and methanolic sodium hydroxide.

(c) Use of ethanolic bark extracts as natural dye : The bark of *Cassia siamea* and *Cassia fistula* are major source of natural dye because of the presence of anthraquinone pigments. Hence, this investigation was carried out to revive the old art of dyeing with natural dyes. The skeins of wool were soaked in clean tap water for half an hour. The optical density was measured by an UV-Vis spectrophotometer at 380 nm.

The dye liquor was prepared by taking 50 g of dye powder bark of both the plants in a beaker containing 100 ml of ethanol. Beakers were simmered at 50–60 °C then brought to boiling for 1 h, cooled, strained to obtain dye liquor 1 (from *C. fistula*) and dye liquor 2 (from *C. siamea*). Various concentrations of both the extracts were placed in beaker containing 100 ml of water. The wool samples weighing one gram each were dyed in different concentrations of dye liquor solutions. The optical density of left over dye solutions were recorded.

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