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Note

Identification of natural red dyes in old Indian textiles

Evaluation of thin-layer chromatographic systems

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The art of textile dyeing in India goes far back into antiquity, with the development of fixing dyes on fabrics with the use of mordants. Many old dyed textiles are now housed in various museums, but are subject to deterioration owing to progressive fading of the dyes and decay of the support.

The two phenomena are linked with the nature of the dyes used and with the reactions between the dyes and the support. In order to resolve these problems, it was considered necessary to acquire a greater understanding to the dyes present on the fabric. First, work on the identification of red and yellow dyes has been undertaken, and this paper deals with red dyes.

A survey of literature on natural dyes and dyeing[1–10] reveals that those listed in Table I were commonly used in India to produce red and related colours. The

TABLE I

NATURAL RED DYES COMMONLY USED FOR DYEING OLD INDIAN TEXTILES

Dyestuff	*Common name*	*Part employed*	*Colouring principle*
Rubia cordifolia Linn.	Munjistha or munjeet	Roots and stem	Munjisthin, purpurin
Morinda citrifolia Linn.	Al or soranji	Root and root bark	Morindone soranjidiol
Morinda spp.	Al or soranji	Root bark and heart wood	
(a) *Morinda tinctoria* Roxb.			
(b) *Morinda umbellata* Linn.	Al or soranji	Root bark and stems	Morindone soranjidiol
Oldenlandia umbellata Linn.	Chay root	Root	Alizarin
Lawsonia alba Lam.	Mehndi henna	Leaves	Lawsone
Ventilago Madraspatana Gaertn.	Ventilago	Root and root bark	Ventilagone
Arnebia nobilis Rach.	Ratanjot	Root and root bark	Alkannin
Carthamus tinctorius Linn.	Safflower	Flowers (red part)	Carthamone
Laccifera lacca Kerr.	Lac insect	Female insect	Laccaic acid
Kermococcus illicis	Kermes	Wingless female insect	Kermesic acid
Dactylopius coccus	Cochineal	Female insect	Carminic acid
Caesalpinia sappan Lin.	Sappan wood	Heart wood	(Brasilin) brasilein
Pterocarpus Santalinus Linn. F.	Red sanders	Wood	Santalin

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colouring principles from most of these dyes were extracted from dyestuffs in weakly alkaline media of sodium hydrogen carbonate or sodium carbonate.

Much research on natural pigments has been carried out and comprehensive texts[11–15] are available. It is clear that most red dyes are derivatives of quinones, and anthraquinones, naphthoquinones and benzoquinones (Figs. 1–3) give strong, red mordant dyes. The red colouring principle of safflower (*Carthamus tinctorius*), previously known as carthamin or carthamic acid[11], was renamed carthamone. Perkin and Hummel[16] were the first to study the chemistry of the red dye principle from the root bark of ventilago (*Ventilago madraspatana*). They named the compound ($C_{15}H_{14}O_6$) ventilagin but could not establish the structure, which is still unknown.

It is also interesting that the wood of sappan (*Caesalpinia sappan*) was used to obtain red dye. The colouring principle is brazilin, a neoflavinoid. Brazilin is unstable and is easily oxidised by atmospheric oxygen to brazilein, a quinone methide[17], the structure of which is similar to that of quinone (Fig. 4).

Thin-layer chromatography (TLC) has been applied to the identification of dyes in European textiles of artistic and historical value[18–21]. The TLC systems reported have limited scope for identification of natural red dyes of Indian origin, based on a variety of plants and animals (*e.g.* insects such as *Kermococcus illicis* and *Lacciferra lacca*). Therefore, in the first instance it was felt necessary to establish the TLC system that would be most suitable for their identification.

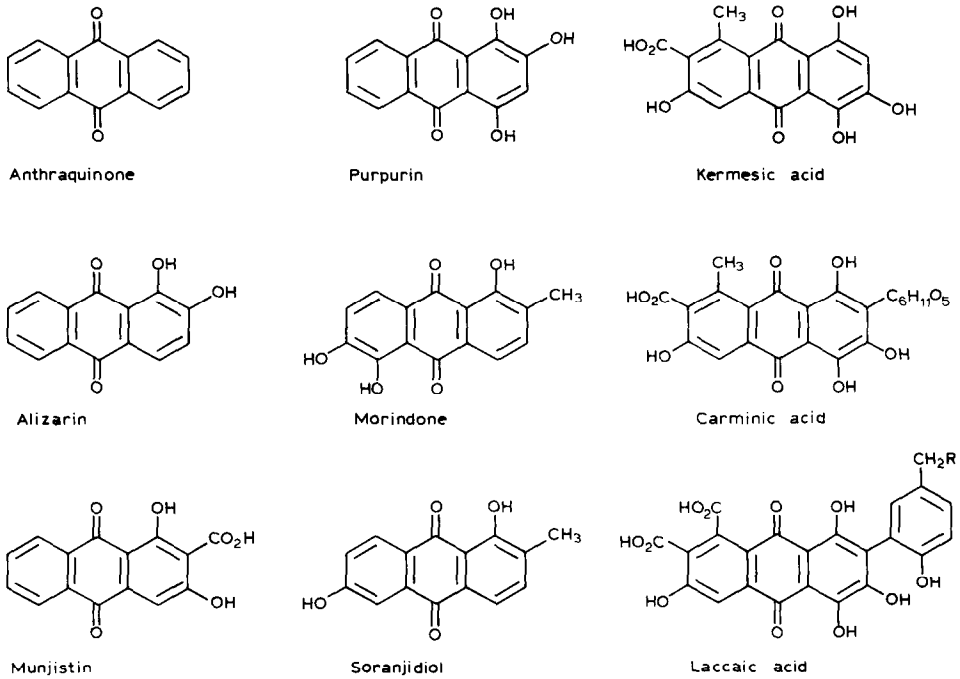

Fig. 1. Dye structures: the basic structure of anthraquinone is found in the following natural red dyes: alizarin from chayroot (*Oldenlandia umbellata*); purpurin and munjistin from munjeet (*Rubia cardifolia*); morindone and soranjidiol from Al or soranji (*Morinda citrifolia* or other species such as *tinctoria* and *umbellata*); kermesic acid from kermes (female insect of *Kermococcus illicis*); carminic acid from cochineal (*Dactylopius coccus* insect); laccaic acid from lac (*Lacciferra lacca* female insect).

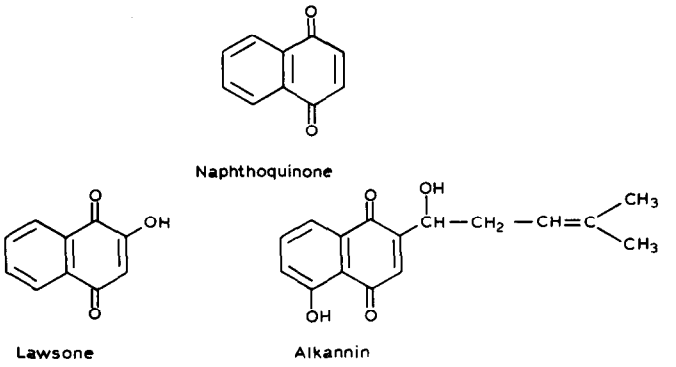

Fig. 2. Dye structures: the basic structure of naphthoquinone is found in lawsone, the red dye from henna leaves (*Lawsonia alba*), and in Alkanin from root and root bark of rantanjot (*Arnebia nobilis*).

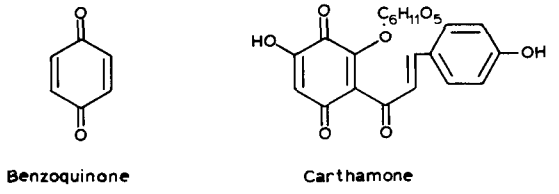

Fig. 3. Dye structures: the basic structure of benzoquinone is found in carthamone, the red dye from the floret of safflower (*Carthamus tinctorius*).

Several TLC systems for the separation of naturally occurring quinones have been reported[22–27]. Many solvent systems were screened initially and those in which dye samples migrated were used for this study.

The purpose of this study was to find a suitable TLC system for the identification of natural red dyes in old Indian textiles.

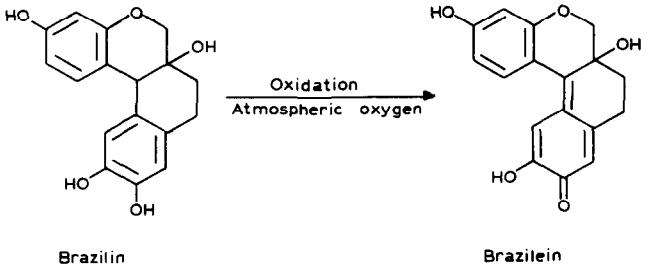

Fig. 4. Brazilin, the colouring principle of sappan wood (*Caesalpinia sappan*). It is oxidized in atmospheric oxygen to brazilein, responsible for the red colour in textiles.

EXPERIMENTAL

Preparation of samples

Five red dyes, namely (i) munjeet (*Rubia cordifolia*), (ii) lac (*coccus lacca*), (iii) *ventilago madraspatana* (all supplied by the Regional Technical Development and

Design Centre, Bangalore), (iv) sappanwood (*Ceasalpinia sappan*) and (v) henna (*Lawsonia alba*) and (both purchased in the local market in Lucknow) were studied.

Amounts of 5 g of powdered dyes were mixed in a beaker with 0.5 g of sodium hydrogen carbonate and extracted with a sufficient volume of water on a water-bath at about 80°C for 1–2 h. The extract was filtered into a separate beaker. The procedure was applied to all the dyes except the sappan wood, the extraction of which was carried out only with water. Wool fibres were mordanted in alum solution and dyed with the extracts of the dyes.

A fibre approximately 1–2 cm long and 0.2 cm in diameter, removed from a textile sample, was placed in a small test-tube, 2–3 ml of 10% hydrochloric acid were added and the tube was boiled on water-bath for about 30 min. The tubes were then placed in a vacuum dessicator to remove any traces of hydrochloric acid. After complete removal of hydrochloric acid, the dye from the fibre was extracted with 1–2 ml of analytical-reagent grade methanol.

Standards

Solutions were prepared by dissolving 1-mg amounts of standards in 1 ml of analytical-reagent grade methanol.

TLC solvent system

A silica gel layer was preferred in this study and solvent systems were chosen according to the literature[22–27] and screened initially to ensure the suitability of the systems for the separation of the dye samples on a glass microscope slide coated with silica gel. Fourteen solvent systems were selected for detailed study (Table II).

TABLE II

TLC SOLVENT SYSTEMS USED IN THE EVALUATION OF SYSTEMS FOR THE IDENTIFICATION OF NATURAL RED DYES

No.	*Components*	*Composition*
I	Ethyl acetate–methanol–water	100:16.5:13.5
II	Isopropanol–ethyl acetate–water	40:40:30
III	Benzene–carbon tetrachloride–acetic acid	50:75:0.8
IV	Benzene–acetic acid	66:33
V	Chloroform–95% ethanol–water	60:30:2
VI	Benzene–methanol	90:10
VII	Chloroform–methanol	90:10
VIII*	*n*-Propanol–ethyl acetate–water	40:40:30
IX	Light petroleum (b.p. 60–80°C)–ethyl acetate	70:30
X	*n*-Butanol–*n*-propanol*–2 *N* Ammonia solution	10:60:30
XI	Benzene–ethyl formate–formic acid	74:24:1
XII	Chloroform (saturated with 25% ammonia)–methanol	70:30
XIII	Toluene (saturated with 25% ammonia)–methanol	40:10
XIV	Toluene–ethyl acetate–methanol	85:10:5

* *n*-Propanol of laboratory-reagent grade was used because of the non-availability of analytical-reagent grade material.

TLC procedure

A 24-g amount of silica gel G was placed in a conical flask with 48 ml of distilled water. The mixture was shaken throughly for 2–3 min to prepare a slurry, which was applied on glass plates with the help of an applicator. The thickness of the layer was 0.25 mm. The plates were allowed to dry at room temperature for about 2–3 h, then activated in an oven at 110°C for about 30 min. The plates were stored in a wooden cabinet over blue silica gel as drying agent.

The solutions containing the extracted dye and standards were spotted with a 5-μl microcapillary on to silica gel. A total volume of approximately 5–10 μl was spotted. Drying was effected with the help of a hand-held dryer. After spotting, the plates were kept in an oven for 10 min and developed until the solvent front reached the 10-cm mark. The plates were sprayed with 10% potassium hydroxide solution and viewed under ultraviolet light at 254 nm. The thin-layer chromatograms were recorded by the graphical copying method.

RESULTS AND DISCUSSION

The resolving power of the individual solvent systems was evaluated by their ability to resolve the samples and standards. The results were interpreted visually and results were expressed as good separation, very good separation, trailing at the start, moved with the solvent front or no separation. A comparison of the resolving powers of the fourteen selected solvent systems is given in Table III. It can be seen that system XI (benzene–ethyl format–formic acid, 74:24:1) has the best resolving power and gives a clear separation of all five natural red dyes.

A thin-layer chromatogram is shown in Fig. 5. In sample 1, there were three major bands; the middle band can be compared with standard 7 (purpurin), but the other two bands could not be identified. Likewise, sample 4 of sappanwood can be

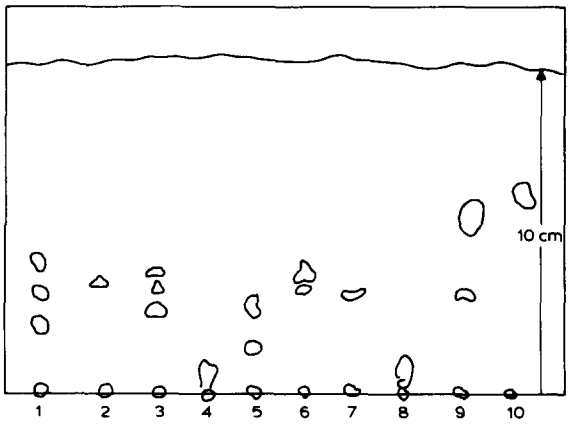

Fig. 5. Thin-layer chromatogram of natural red dyes. Adsorbent, silica gel G; solvent system, XI (Table II), benzene–ethyl formate–formic acid (70:24:1); run, 10 cm; detection, spraying with 10% methanolic potassium hydroxide and observation under UV light. 1 = Munjeet or munkjistha (*Rubia cordifolia*); 2 = lac (*Laccifera lacca* female insect); 3 = ventilago (*Ventilago madraspatana*); 4 = sappan wood (*Caesalpinia sappan*); 5 = henna, mehndi (*Lawsonia alba*); 6 = alizarin; 7 = purpurin; 8 = brazilin; 9 = lawsone; 10 = emodin.

TABLE III

COMPARISON OF THIN-LAYER CHROMATOGRAMS DEVELOPED WITH THE 14 SOLVENT SYSTEMS USED IN THE EVALUATION STUDIES FOR THE IDENTIFICATION OF FIVE NATURAL RED DYES

+ + + = very good separation; + + = good separation; + = trailing at the start; + – = moved with the solvent front; – = no separation.

Dye	*Solvent system**													
	I	*II*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*	*IX*	*X*	*XI*	*XII*	*XIII*	*XIV*
Munjeet	–	+ –	+	–	+	–	–	+ –	–	+ –	+ + +	+ –	+ –	+ +
Lac	–	+ –	–	–	+	–	–	+	–	–	+ + +	+ –	+ –	+ +
Ventilago	–	+ –	+	–	–	–	+	–	+	–	+ + +	–	–	–
Sappan wood	–	+ –	–	+	–	–	–	–	–	–	+ +	–	–	–
Mehndi	–	–	–	–	–	–	+	–	+	–	+ + +	–	–	–
Standards:														
Alizarin	–	+ –	–	+	+	–	–	+ –	–	+ –	+ + +	+ –	+ –	+ +
Purpurin	–	+ –	–	–	+	–	–	+ –	–	+ –	+ + +	+ –	+ –	+ +
Brazilin	+ +	–	–	+	–	–	–	–	–	–	+ +	–	–	–
Lawsone	+ +	–	–	+ +	–	+	+	–	+	–	+ + +	–	–	–
Emodin	+ +	–	–	+ +	–	+ +	+ +	–	–	–	+ + +	–	–	–

* For the compositions of solvent systems I–XIV, see Table II. The adsorbent for all the solvent system used was silica gel G

compared with standard 8 (brazilin). Sample 5 had two bands, one of which could be identified with the lower band of standard 9 (lawsone).

CONCLUSIONS

A silica gel layer and the solvent system benzene–ethyl formate–formic acid (74:24:1) can resolve minor and major components in textile dyes, with the formation of definite patterns on the TLC plate. It is necessary to spot the extracted dyes from the questioned and standard fibre samples on the same plate so that a side-by-side comparision of the separated dye components can be made.

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