Pak. J. Sci. Ind. Res. 2005 **48**(6) 430-432

Short Communication

Spectroscopic and Dyeing Characteristics of the Yellow Dye from *Morinda lucida* (Brimstone Tree)

A. O. Adetuyi*, L. Lajide and A. V. Popoola
Department of Industrial Chemistry, Federal University of Technology, Akure, Ondo State, Nigeria

(received December 11, 2003; revised October 10, 2005; accepted October 15, 2005)

Abstract. The yellow dye obtained from *Morinda lucida* plant, yield 16.5%, melting point 108-110 °C, showed absorption in the visible range 400-450 nm. Four major functional groups were identified at λ_{max} of 435 nm. The IR and ^{1}H-NMR spectra exhibited absorptions consistent with a conjugated polyfunctional structure. The yellow morinda dye is tentatively proposed as 4-benzoyl-2-amino acetaldehyde. The pigment imparted its brilliant yellow hue on the dyed cellulosic yarn and fabric with moderate fastness ratings to washing, perspiration, hot-pressing, however, having poor stability to high energy radiation.

Keywords: brimstone tree, *Morinda lucida*, yellow hue, equilibrium dye uptake, initial modulus, yellow morinda dye

Morinda lucida plant (brimstone tree), Family Rubiaceae, is sold in the Southern Nigerian markets for its medicinal uses (Burkill, 1985). Adesogan (1973) isolated oruwal as anthraquinols and oruwalol, as 5- or 8-hydroxyl derivatives of oruwal, and 10 anthraquinones from the stem of the plant. The plant is a yellow wood when fresh, which however darkens on exposure, becoming dark-brown with lighter yellowish-brown sapwood. It is locally called 'orowo' or 'awopa' in Southern Nigeria. It is also used, like the teak tree (*Tectona grandis*), for household construction in Western Africa and Southern Nigeria. A yellow dye is associated with all parts of this plant, and the dye extraction and purification from the bark of the plant has been reported earlier (Adetuyi *et al.*, 2002). The present study attempts to elucidate the structure of the yellow morinda dye, using spectroscopic methods, such as UV-visible and nfra-red (IR), and proton-nuclear magnetic resonance (^{1}H-NMR). The study further reports its dyeing properties on cellulosic fibres.

Scoured and bleached white cellulosic fibres (yarn and fabric) were used for studies on the dyeing characteristics of morinda yellow pigment without prior application of a mordant. The dyeing was done at two different depths, 2% and 5% for cotton yarn and fabric, respectively, in an infinite dyebath in which the concentration of the colourant was maintained constant (Giles, 1974).

Two dyebaths, each containing 4 g/l of the yellow morinda dye extract (2.5 ml) and dye assistants: 30% sodium chloride (5 ml) and 3% sodium hydroxide (10 ml) in a liquid-to-goods ratio of 100 : 1, and a blank bath of the same liquor ratio having the same contents but without the addition of pigment were prepared for 2% dyeing of 500 mg cotton yarn (Giles, 1974). The dilution factor for the dye stock was 20. One dyebath served as the standard solution from which various aliquots were taken for serial dilutions. Their optical density was measured on Biochron-4060 spectrophotometer at λ_{max} 402 nm of the pure dyestuff solution. The dyeing was done in a single-bath dyeing machine MBMK II at temperatures of 60 °C and 80 °C. Sampling of the spent dye-liquor, about 2 ml, was taken at intervals of 30 min for a period of 3 h. The dyed yarns were removed from the dye-liquor prior to sampling. Equivalent aliquot from the blank liquor was introduced into the dye liquor to replace the dye assistants (which were added to the pigment to aid dye solubilization and dyeing), that had been removed by the dyed yarn. The dyed yarns were returned and the dyeing was continued till the next sampling period. The sampled solutions were diluted and their optical density was measured. The dye-uptakes were determined using the following formula:

$$\frac{1000 \times C_{Df}}{W_{Df}} \qquad (1)$$

where:

W_{Df} = weight of the dyed cellulosic yarn (0.5 g)

C_{Df} = the percent concentration of dye in yarn (w/v), which was calculated as follows:

$$C_{Df} = 0.02 - C_{Ds} \qquad (2)$$

where:

0.02% (%w/v) = a constant (initial concentration of dye-liquor)

---

*Author for correspondence; E-mail: yomiadetuyi2002@yahoo.com

C_{Ds} = the concentration of spent dye-liquor at various time intervals of dyeing, calculated from the calibration curve

After dyeing, the yarn samples were removed, washed properly in a mild soap solution, rinsed in cold distilled water, and dried. The load-elongation curves of the dyed cellulosic yarn of various lengths were determined at constant-rate-of-elongation of 500 mm per min and 500 N per tension, using Instron tensile tester T5000.

A 5% dyeing of cellulosic fabric (6 g) and the assessment of fastness properties were also done in a dyebath, containing 30 ml of the dye solution (1 g/100 ml) and dye assistants: 30% sodium chloride (18 ml) and 5% sodium hydroxide (6 ml) in a liquor ratio of 30 : 1 for 3 h at 60 °C (Giles, 1974). Assessment of four fastness properties, namely, washing, perspiration, hot pressing (heat treatment), and fastness to light were carried out on the dyed fabric in accordance with the International Standards Organisation (ISO) procedures (SDC, 1992).

A low dyeing temperature of the 60 °C favours dye absorption on the yarn. The dye molecules were well retained in the accessible regions (amorphous) of the yarn, which lead to high dye uptakes. This was evident in the higher value noated (5.67 N/Tex) of the initial modulus (the slope of the stress-strain curve at the origin) of the dyed yarns at 60 °C.

The bleached cellulosic fabrics were uniformly and evenly dyed, appearing as the yellow hue of moderate fastness ratings of 2.5, 3.2 and 4.5 to washing, perspiration and hot pressing, respectively. The fabrics, however, showed poor stability to high energy radiation as compared to the standard dye (procion yellow R).

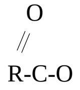
The UV-visible absorption spectrum of the pure dye measured in methanol was observed to be in the visible range of 400-450 nm having λ_{max} 435 nm. This is a characteristic of a yellow hue corresponding to the absorption of violet/blue light from the dye. This yellow hue was detected on post-column run on TLC plates, with R_f value of 0.63, m.p. 108-110 °C (Adetuyi *et al.*, 2002). This absorption of the dye in the visible region conferred the presence of colour imparting chromophores in the dye as the unsaturation system. This unsaturation (carbon-double bonds) must be fairly conjugated and extended within the chromogen. The more extended the conjugated double bond system is, the smaller the excitation energy required for TT → TT* transition to occur, and the wavelength of maximal absorption increases thereby affecting the observed colour changes from yellow→orange→ red→purple (Kemp, 1991).

The results of the major characteristic absorption peaks and the approximate chemical shift positions of the observed peaks in IR and ^{1}H-NMR spectra are presented in Tables 1 and 2, respectively. Both the Tables showed similarities of functional groups. Hydroxyl, possibly due to hydrogen bonding (3560 - 3200 cm, δ 10.0); aliphatic (2970 - 2880 cm, δ 1.2); carbonyl (1700 - 1690 cm, δ 9.0); and aromatic (1600 - 1460 cm, 850 - 750 cm, δ 7.2 - 7.8). A chemical test on the pigment indicated the presence of amines because it was soluble and insoluble in hydrochloric acid and $NaHCO_3$, respectively. It was also positive to nitrogen detection, using sodium-fusion test. With the spectroscopic data obtained in the present studies, aided with the informa-

Table 1. Infra-red spectral analysis of the yellow morinda dye extract obtained from *Morinda lucida*

Absorption frequencies (cm^{-1})	Mode of vibration	Comments
3560 - 3200	broad bonded O-H_{str}	hydroxyl group of alcohol/phenolic compounds
2970 - 2800	C – H_{str}	saturated hydrocarbon
1700 - 1690	C = O_{str}	carbonyl group in carboxylic acid
1600 - 14600	C = C_{str}	alkene/aromatic ring
1370 - 1250	C – N_{str} or C –O_{str}	aromatic amines or alcohols
850 - 750	weak C – H out-of-plane deformation	aromatic *ortho* substitutents

Table 2. ^{1}H-NMR approximate chemical shifts of the *Morinda lucida* dye extract (fraction cc)

Chemical shifts (absorptions) δ	Multiplicity	Comments
0.8 - 1.2	complex	proton of aliphatic group CH_3–C–
2.2		solvent - acetone
3.0		solvent - water
3.4 - 4.2	complex	proton of methoxyl group CH_3–O
5.3	triplet	proton of CH_2–O
7.2 - 8.2	singlet	proton of aromatic benzene ring
9.0	singlet	proton of aldehde H–C=O
10.0	singlet	proton of bonded hydrogen  $R\text{-}\overset{O}{\overset{/\!/}{C}}\text{-}O$

tion reported in literature (Pine *et al*., 1991; Banks *et al*., 1980), a structural formula of $C_9H_8NO_2$, named as 4-benzoyl-2-amino acetaldehyde, is tentatively proposed for the yellow colouring pigment from the brimstone tree (*Morinda lucida*).

Acknowledgement

Authors would like to express their gratitude to the Federal University of Technology, Akure, Nigeria, Research Grants Committee for their support.

References

Adesogan, E.K. 1973. Anthraquinones and anthraquinols from *Morinda lucida:* biogenetic significance of oruwal and oruwalol. *Tetrahedron* **29:** 4099-4102.

Adetuyi, A.O., Popoola, A.V., Lajide, L. 2002. Isolation, purification and UV-visible spectroscopic study of the colourant from *Morinda lucida* plant. *J. Appl. Sci.* **5:** 3174-3185.

Banks, R.C., Matjeka, E.R., Mecer, G. 1980. *Introductory Problems in Spectroscopy,* pp. 1-31, The Benjamin-Cummings Publishing Comp., Inc., London, UK.

Burkill, H.M. 1985. *Revision of Dalziel's Useful Plants of West Tropical Africa*, vol. **1,** pp. 111-112, 2nd edition, White Friars Ltd., London, UK.

Giles, C.H. 1974. *A Laboratory Course in Dyeing,* pp. 65, 126-127, 3rd edition, The Society of Dyers and Colourists, Bradford, UK.

Kemp, W. 1991. *Organic Spectroscopy,* pp. 245-248, Macmilan Publ., Ltd., London, UK.

SDC. 1992. *Standard Methods for the Determination of the Colour Fastness of Textiles and Leather,* 3rd edition, The Society of Dyers and Colourists Publication, Bradford, UK.

Pine, S.H., Hendrickson, J.B., Cram, D.J., Hammond, G.S. 1981. *Spectroscopic Organic Chemistry,* pp. 1-130, 4th edition, McGraw-Hill International Book Company, Singapore.