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## EXTRACTION, SPECTROSCOPIC AND COLOURING POTENTIAL STUDIES OF THE DYE IN GINGER RHIZOME (*ZINGIBER OFFICINALE*)

A. V. POPOOLA, K. O. IPINMOROTI, A. O. ADETUYI AND T. O. OGUNMOROTI

Department of Industrial Chemistry, Federal University of Technology, PMB-704, Akure, Ondo State, Nigeria

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The dye in the rhizome of the plant, *Zingiber officinale* was extracted quantitatively using the solid-liquid extraction method and its physico-chemical parameters as well as colouring potential studied. A lustrous, powdery brown dye melting point Ca. 88-90° of 13.90% yield was obtained. The dye was soluble in hydroxyl organic solvents and gave one homogenous component of  $R_f$  value of 0.86 on chromatographic separation and a wavelength of maximum absorption  $\lambda_{max}$  420nm. The IR spectrum of the dye showed three major functional groups, of OH group with broad band absorption between 3405-3120  $cm^{-1}$ , aliphatic or saturated C-H stretching at 2900-2880  $cm^{-1}$  and C=O peak at 1710-1700  $cm^{-1}$  whilst the presence of 1,4-disubstitution on benzene ring was observed at 1930-1880  $cm^{-1}$ . Major proton absorptions on  $^1H$ -NMR were observed at 7.2 ppm, 3.9 ppm and 1.2 ppm signifying the presence of benzyl, hydroxyl and ethyl protons at these respective absorptions. The dye gave a brilliant yellow colouration of light, wash and dry ironing (pressing) ratings of 5, 3 and 4 respectively on bleached cotton fabric.

**Key words:** Ginger, Annatto, Lassaigne test, Mordant.

### Introduction

Dyestuffs of vegetable origin were perhaps discovered as a result of accidental staining from berries, nuts, roots or other plant parts. Dyes have long been used for a number of purposes including painting of pictures in caves, dyeing of various articles of clothing and used as cosmetics for body adornment. The ancient Carribean Indians used the popular red dye annatto as cosmetic to stain their bodies, ultimately to frighten off their adversaries during times of aggression.

Recently, some natural dyes especially those from edible, non-toxic substrates have found increasing use as food and drug colours. A list of such speciality colourants can be found in relevant literatures [1]. The list of such natural dyes used for this end-application is diverse. Among the very common ones used today in modern food, drug and cosmetic industries are those found in: *Bixa orellana*, *Cola nitida*, *Zingiber officinale*. Their use has become such a part of man's custom that it is difficult to dissociate them from modern chemical and allied industries.

The plant ginger (*Z. officinale*) of the family Zingiberaceae was one of the spices introduced into Europe and for a long time was next in importance to pepper. The rhizomes were used for flavouring food and beverages and to a lesser extent as ingredient in medicinal preparations. The dye obtainable from ginger is extracted from the dried rhizomes usually by one of the common techniques used for removing pigments from solids by solvent extraction.

In the present study, following extraction of the pigment from the rhizome, it was purified using chromatographic techniques and attempt at resolving its structure studied using

UV/visible,  $^1H$ -NMR and IR techniques. The dyeing properties of this pigment on textiles have not been given much attention previously. Consequently, its potentials to be used as a textile colourant was investigated.

### Materials and Methods

The ginger used for the project was purchased of markets in Akure township, Ondo-state Nigeria. The ginger rhizomes were chopped into smaller pieces and sundried for 3 days. Further drying was, however, done in the oven at 105° for 6 hrs to reduce its moisture content considerably before extraction.

**Extraction of the ginger oil and the colourant.** Ginger contains both the ginger oil and the colourant, in order to collect the colour oil free, the oil has to be removed first by extracting with *n*-hexane.

To remove the oil, the sample was finely grounded. 8Grams of the sample was collected in a thimble, 250 ml round bottom flask containing *n*-hexane was set up with soxhlet extractor, the thimble containing the sample was put in the extractor and the apparatus was set up on the electrothermal extraction unit. Extraction of the oil was done for 4 hrs under moderate boiling and the flask was cooled. The flask was removed and the solvent contained in it was recovered by distillation.

To remove the colourant, methanol was used as the solvent for extraction as against *n*-hexane for the oil. The colourant was extracted for a period of 4 hrs using the same method described for the oil and the extractant was equally recovered by distillation. The colourant obtained after the

distillation was cooled, dried and recrystallised in ethanol.

*Determination of physico-chemical properties.* The following physico-chemical properties were determined for pure colourant.

*Solubility test and melting point.* Solubility test of the ginger colourant was carried out in some selected solvents. The following solvents were used: methanol, ethanol, glycerine, water, groundnut oil and propylene glycol. The test was carried out by adding 10 mg of the colourant to 5ml of each of the above solvents in test tube. Where the colourant was not soluble in the cold, a gentle heat was applied by placing the test tube inside a heated water bath. Melting point of the pure colourant was determined on hot stage microscope.

*Lassaigne test.* About 20 mg of the colourant was heated together with some quantity of sodium in an ignition tube, gently at first and then more strongly to dull redness. The tube, while still hot, was plunged into about 15ml cold distilled water in an evaporating basin. The mixture was boiled for a short time stirred and filtered. The clear filtrate was tested for the presence of nitrogen, sulphur and the halogens.

*Purification of the colourant using TLC technique.* The colourant was fractionated by column chromatography over alumina in a glass column. The sample was dissolved in minimum amount of methanol and gently introduced on top of the column. The compounds were eluted using solvents of increasing polarity as follows: S<sub>1</sub> Hexane, 200ml. S<sub>2</sub> Hexane: Benzene, (80:20 v/v) 200ml. S<sub>3</sub> Benzene, 200ml. S<sub>4</sub> Benzene: Chloroform, (75:25 v/v) 200ml. S<sub>5</sub> Benzene: Ethanol, (80:20 v/v) 200ml. S<sub>6</sub> Benzene: Ethanol, (60:40 v/v) 200ml. S<sub>7</sub> Benzene: Ethanol, (20:80 v/v) 200ml. S<sub>8</sub> Ethanol, 200ml.

About 25 fractions were collected and examined by T.L.C. (Thin Layer Chromatography) in chloroform: acetone (90:10 v/v) for 10 mins and spots detected with sulphuric acid-nitric acid reagents and bromocresol green.

*Spectroscopic studies.* Ultraviolet spectroscopy, Infra-red and Nuclear Magnetic Resonance investigations of the colourant were carried out. The IR and U.V spectra were run on SP<sub>3</sub>-300 IR Spectrophotometer and SP<sub>8</sub>-4000 UV/Visible spectrophotometer respectively. The NMR spectrum was run on JEOL 270 Instrument.

*Dyeing of cotton fabric and assessment of fastness properties.* 100 Percent cotton fabric, scoured and bleached white was used for the dyeing without prior application of a mordant. The dyeing was carried out in an 'infinite' dyebath in which the concentration of the colourant was assumed constant [2]. Dyeing was allowed to proceed for 1 hr. after which the fabric was removed from the dye bath and properly washed in a mild soap solution before being rinsed in cold distilled water, dried and subsequently fixed with hot iron.

Assessment of 3 fastness properties, i.e. light, washing

and dry ironing was carried out on the dyed fabric according to the International Standard for Organisation's procedure described in an earlier publication [3]. Under each test, 10 specimens of the dyed article were tested and the mean value of the results obtained taken as the fastness rating for the test.

## Results and Discussion

*Physico-chemical properties.* The results of the physico-chemical tests carried out on the dye extract are summarised in Table 1.

*Column and thin layer chromatography results.* The results of the fractionated pools collected from column chromatography are shown in Table 2. On T. L. C results, the fractions AA, CC, DD and EE gave a single yellow spot (reddish/brown with H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> spray) of R<sub>f</sub> value of 0.86. This shows that the extract obtained did not contain multicomponents characteristic of a mixture.

*UV/Visible results.* The results of the absorption spectra of the crude and the purified dye extracts are shown in Figs. 1 and 2 respectively where a single wavelength of maximum absorption  $\lambda_{max}$  value of 420 nm is seen in both spectra. The UV/Visible absorption at  $\lambda_{max}$  420nm which falls within the

TABLE 1. PHYSICO-CHEMICAL PARAMETERS OBTAINED FOR DYE FROM GINGER (*ZINGIBER OFFICINALE*).

Tests performed	Results
Appearance of crystals	Light brown lustrous crystals.
Yield	13.96%
Melting point	80-90°
Solubility	Solvent Ethanok, Propanol, Acctone and Benzene - Soluble in all proportions. Chloroform, Hexane and Ethyl acetate - Partially soluble. Distilled water and Pet.Spirit - Insoluble.
Lassaigne's sodium Fusion test.	Nitrogen, Sulphur and Halogens - Absent.

TABLE 2. POOLED FRACTIONS COLLECTED FROM COLUMN CHROMATOGRAPHY.

Solvent system	Code No.	Fractions	Weights (g)	R <sub>f</sub> values
S <sub>1</sub> , S <sub>2</sub>	AA	1-6	0.1320	0.86
S <sub>2</sub> -S <sub>4</sub>	BB	7-13	-	-
S <sub>5</sub>	CC	14-17	0.2751	0.86
S <sub>6</sub> , S <sub>7</sub>	DD	18-22	0.1542	0.86
S <sub>7</sub> , S <sub>8</sub>	EE	23-30	0.2096	0.85

visible region of the electromagnetic spectrum shows the presence of a colour imparting chromophore in the dye extract. The chromogen itself may be a polynuclear hydrocarbon compound or a simple aromatic with conjugated side chain. It also indicates that the dye extracts in the various fractions have the same hue [4], hue being the predominant colour transmitted by an organic pigment when the complimentary colour contained in the light passing through it has been absorbed. The hue of a colour is determined by the predominant wavelength of absorption in it. The absorption of the compound at  $\lambda_{\text{max}}$  420nm corresponds to the absorption of violet light by the sample leaving its complementary colour, yellow to be transmitted by the dye [5].

The quality of the colour of the extract is a product of the sharpness of its absorption spectrum which in this case is represented by the narrow range of the intensity profile. The absorption of a narrow absorption band for sample CC in the spectrum (Fig. 2) accords with the brightness of the dye sample.

*Infra-red results.* The Major characteristic absorption peaks observed in the IR spectra of the dye are shown in Table 3. There is the presence of hydroxyl group (-OH) due to the broad absorption frequency recorded between 3405-3120 $\text{cm}^{-1}$ . Absorption in the region 2920-2880 $\text{cm}^{-1}$  is due to aliphatic or saturated C-H stretching. A series of weak bands were observed between 1930-1880 $\text{cm}^{-1}$  indicating the presence of substituents on the benzene ring whilst the band at 1710-1700 $\text{cm}^{-1}$  is characteristic of a carbonyl group. The peaks observed in the region 1630-1430 $\text{cm}^{-1}$  are due to benzene ring and the absorption at 830-720 $\text{cm}^{-1}$  indicates a para-substitution on the benzene ring.

*Nuclear magnetic resonance results.* The  $^1\text{H}$  NMR spectrum of the pure dye extract is shown in Fig.3. The major chemical shifts of the observed peaks are contained in Table 4. The proton signals at 1.2 ppm (parts per million) with triplet or quartet multiplicity is due to ethyl group (- $\text{CH}_2\text{CH}_3$ ). The NMR also indicates the presence of benzene ring with proton signal at 7.2 ppm. The hydroxyl group at 3.9 ppm and the protons of the alkene groups at 3.8 and 6.5 ppm. All are jointly attached to the benzene ring.

*Fastness properties of the dyed fabric.* The results obtained for the fastness ratings of the dyed fabric are contained in Table 5. The mean fastness to light rating of 5 obtained on a scale of 8 can be considered good. This shows that the dye structure itself is fairly stable to high energy radiation such as ultraviolet. This fact lends credibility to the inference drawn under the uv/visible results that the chromogen responsible for the colour in the the dye structure may as well be a polynuclear compound or an aromatic nucleus having conjugated side chain since a lower fastness to light rating will be expected for

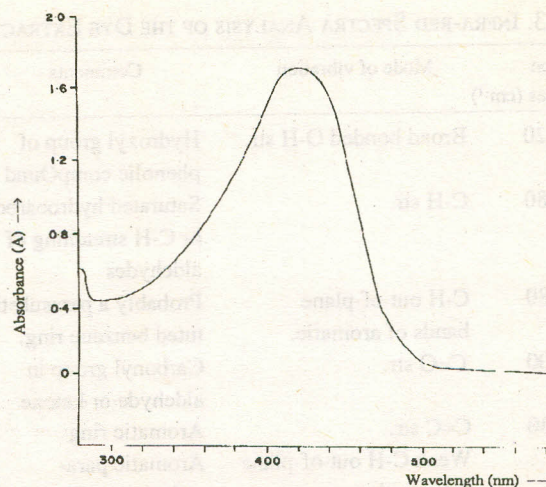


Fig. 1. Electronic absorption spectrum on the crude dye extract (Sample A).

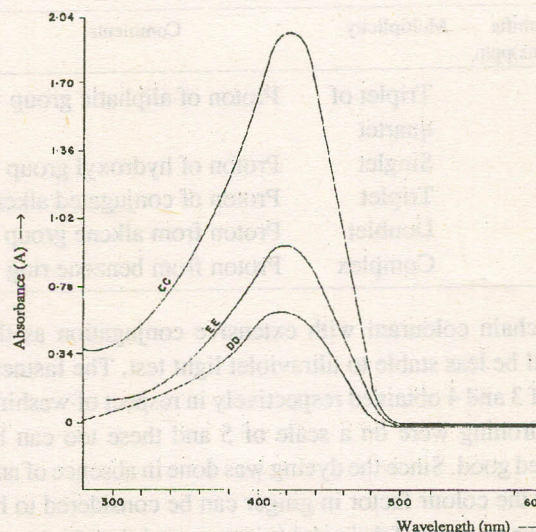


Fig. 2. Electronic absorption spectrum on the purified dye extracts (Sample CC, DD and EE).

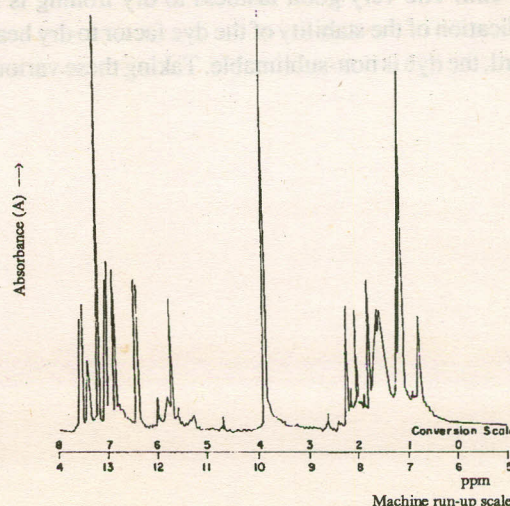


Fig. 3.  $^1\text{H}$  NMR spectrum of the dye extract (Sample A) in  $\text{CDCl}_3$ , 6ppm=0.

TABLE 3. INFRA-RED SPECTRA ANALYSIS OF THE DYE EXTRACT.

Absorption frequencies (cm <sup>-1</sup> )	Mode of vibration	Comments
3405-3120	Broad bonded O-H str.	Hydroxyl group of phenolic compound
2920-2880	C-H str.	Saturated hydrocarbon or C-H stretching of aldehydes
1930-1880	C-H out-of-plane bands of aromatic.	Probably a parasubstituted benzene ring.
1710-1700	C=O str.	Carbonyl group in aldehyde or ketone
1630-1430	C=C str.	Aromatic ring
830-720	Weak C-H out-of-plane deformation	Aromatic para-substituent

TABLE 4. <sup>1</sup>H NMR CHEMICAL SHIFTS OF THE DYE EXTRACT.

Chemical shifts (absorptions)ppm	Multiplicity	Comments
1.2	Triplet of quartet	Proton of aliphatic group
3.9	Singlet	Proton of hydroxyl group
5.8	Triplet	Proton of conjugated alkene
6.5	Doublet	Proton from alkene group
7.2	Complex	Proton from benzene ring

straight chain colourant with extensive conjugation as the latter will be less stable to ultraviolet light test. The fastness ratings of 3 and 4 obtained respectively in respect of washing and dry ironing were on a scale of 5 and these too can be considered good. Since the dyeing was done in absence of any mordant, the colour factor in ginger can be considered to be substantive to cotton fabric and it is expected that the use of any suitable mordant either natural or synthetic will improve this further still. The very good fastness to dry ironing is in itself an indication of the stability of the dye factor to dry heat. In other word, the dye is non-sublimable. Taking these various

TABLE 5. FASTNESS RATINGS OF GINGER DYED COTTON FABRIC (FOR WEARING APPAREL).

Fastness test specimens	Light	Washing	Dry ironing
1	5	2+	5
2	5	3	4
3	4+	3	3
4	5	3	5
5	6	4	3
6	5	3	3
7	5	3	4
8	5	3	4
9	4	3	5
10	6	3	4
Means fastness rating	5	3	4

performance factors into consideration, the dye in ginger rhizome can be recommended for use as textile colourant. The limitation imposed by the yield of the dye vis-a-vis the enormity of such dye needed by the textile industry, however, makes it suitable only for textiles on a handicraft scale. Fabrics so produced having shown good fastness ratings to light, washing and dry ironing will find good use either as wearing or interior furnishing.

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