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LOCAL PLANT DYES AND THEIR APPLICATION IN pH TITRATION, DYEING OF FABRICS AND PAPER

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ABSTRACT

Local gin (50% ethanol/water) extracted 8.5% of orange-reddish dye from the seed of Sterculia tragacantha while methanol extracted 12.1% wine red dye from the rhizome of Zingiber officinale. The IR and the UV absorption characteristics and the results of the chemical analysis indicated that these dyes are of hydroxyanthraquinone class. The dye extract from Sterculia tragacantha gave persistant orange colour to white synthetic fabric (Satin) but stained white paper pink, while extract from Zingiber officinale dyed natural white cotton fabric, paper and satin fabric, bright yellow. The colours were fast to water, washing detergent solutions and to daylight. The dye from Zingiber officinale was also found suitable as colour indicator in pH titration of a strong acid against a strong base, therefore serving as a substitute for the methyl orange standard indicator in volumetric analysis. Recommendation for adoption in practical Chemistry exercises in Secondary Schools is made.

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INTRODUCTION

Man has always shown great ingenuity in his search for colours to express his ideas and feelings, to brighten his surroundings and to decorate himself. Before the introduction of the synthetic dye, mauvaine, from coal tar by Perkin in 1856 (Abrahant, 1977) man had been using colouring materials extracted from natural sources namely, plants, insects, animals and minerals. The list of common colouring extracts from materials and their sources are given in Table 1. Castine'(1975) has also given a list of some dyes obtained from named plant sources. Extraction of coloured materials from plants can be done using the flowers, leaves, fruits, seeds, stems (barks) or the roots.

The people of Akwa Ibom State of Nigeria have been using coloured plant extracts in decorating their bodies. Culturally, women in the fattening rooms mix extract from the seeds of Sterculia tragacantha with palm oil as cream to give light reddish appearance to their skin while the pulp from Zingiber officinale is mixed with clay pigment (ndom) to give it a yellowish tint also used in decorating the body. Dyeing of raffia (ndam) with natural dyes from plants dates back to many centuries and is still being practised in Ikot Ekpene, the Raffia City of Akwa Ibom State.

TABLE 1: Dyes from Some Local Plants

S N	NMAE OF LOCAL (PLANT)	BOTANICAL NAME	PART USED	COLOUR EXTRACTED	USES
1	Awa (cube root)	Lonchocarpus cyanescans	Leaves	bluish-green	cloth dyeing
2	Atan Unen	Zingiber officinale	Rhizome	yellow	dyeing of cosmetics and essential oil
3	Idod	Sterculia tragacantha	Seeds	reddish-orange	dyeing of cosmetics
4	Akukin	Rothmanid whitefield	Fruit and seed	brown on paper and black on skin/hair	as cosmetics dyeing hair black
5	Henno (ibaba)	Lawsoned alba	Leaves, flower	red	dyes for cos-metics and essential oils
6	Corn flower	Centaurea cyanus	Petals	dark red	cosmetics dyes
7	Rose	Rosa gallila	Petals	dark	cosmetics for essential oils

Objectives

The objectives of the study were to:

(a) Extract dyes from local plant sources with suitable solvents.

(b) Characterize the dye extracts.

(c) Use the dye extracts (i) as end-point colour indicator in pH titration and (ii) in dyeing of fabrics and paper.

(d) Recommend the dyes as a resource in curriculum innovation in the teaching of practical chemistry in the Secondary School.

METHODS

(a) Extraction of Dyes

The pods of Sterculia tragacantha (idut) and the rhizome of Zingiber officinale (aran unen) were collected from a school garden in Uyo. The pods of Sterculia tragacantha, were broken to release yellowish red dry seeds which were ground into powder, dried in air and stored in a container (sample A. 70g). the rihizome of Zingiber officinale was washed with water. The exoderm was peeled off and then grated into yellowish pulp, sundried and stored (sample B, 85g) before extraction.

Local gin (~ 50% ethanol/water) was used for extracting dye from sample A, while methanol was most suitable for sample B. Extraction was done with the Soxhlet Extractor using 500cm^3 Extracting Flash. 30g of each sample was refluxed for three hours within which the solvent in the thimble of the extractor became very faint in colour indicating near total extraction of the dye from the crushed sample. The resulting solution was distilled off in a water bath and traces of the solvent removed in a rotary evaporator after addition of diethyl ether. The coloured solid extracts 2.65g (sample A) and 3.63g (sample B) were stored in a dessicator. The yield was 8.5% for sample A and 12.1% for sample B.

(b) Characterization of the Dyes

(i) IR and UV Absorption of the Dyes

1% (W/V) solutions of the extracts were made by dissolving 0.1g of sample A in $10cm^3$ of 98% ethanol and 0.1g of sample B in $10cm^3$ methanol. These solutions were then used in measuring the Infra Red (IR) and the Ultra Violet (UV) absorption pattern in the IR spectrophotometer (Model-Perkin Elmer 710 B) and spectronic 10 Model-Bush and Lomb respectively (William, 1973) (Ethanol and methanol were used as blanks for A and B respectively).

(ii) Chemical Tests for the Functional Groups in Dye Extracts

Chemical tests for the presence of phenolic CH, carbonyl (C=0) group and unsaturation and hydroxyanthra-quinone compounds were carried out and were positive (Vogel, 1968).

(iii) Colour Effect of the Extracts in Acid and Base Solutions

A solution of dye A in excess NaOH solution gave red colour and in excess HCL solution gave-orange colour. Extract B solution was orange in acid and yellow in alkaline solution.

(c) Application of the Dye Extracts

(i) pH Titration with the Dyes

1% (W/V) solution of extract A was prepared in ethanol and 1% (W/V) solution of extract B was prepared in methanol. Three drops of each of the dye solutions A and B were used as indicators respectively in neutralisation reaction between 0.1MHCL and 0.1MnaOH solutions. Extract A gave no sharp end point in direct titration while a sharp end point ($10.95cm^3$) was obtained with B. Titration which B was repeated using pH Meter (Model 7010, Electronic Instruments Limited). The pH against volume of acid plot using dye solution b was compared with that obtained by using methyl orange indicator (Fig. 1). From the plots the pH range of B coincided with the pH range of methyl orange and the general shape of the curve for strong acids with strong alkalis using standard indicators. The theoretical pH range for methyl orange is 3.1 – 4.4 (Vogel, 1979: 54).

(ii) Dyeing of Fabrics and Paper with the Dye Extracts

2% (W/V) solution of each dye was prepared and used in dyeing 3cm × 3cm pieces of white cotton and synthetic (satin) fabric. The dyeing was carried out by dipping the pieces in each dye solution for ten minutes with gentle agitation. The fabrics were dried in air.

Test for fastness

Fastness to Water: Each of the dyed fabrics was soaked in water for one day. Squeezed to remove the excess water and dried in air. The colour of the fabric after being soaked in water was compared with its original colour. (there was no change in the colour of the dyed fabrics).

Fastness to washing with detergent solution was done by washing a piece of dyed fabric in bar soap solution, rinsed in water and dried in air. The resultant colour of the washed fabric was compared with the originally dyed piece. The test was repeated for synthetic detergent (Omo) solution.

Fastness in light was done by exposing the dyed pieces to daylight for 48 hours. After which the colour of the exposed piece was compare with that of the originally dyed fabric.

The dyeing process and fastness in light were repeated with white paper. The resultant obtained are shown in Table 2.

TABLE 2: Dyed Fabric/Paper And Their Fastness Properties

PLANT DYE EXTRACT	WHITE SUBSTRATE	COLOUR AFTER DYEING	FASTNESS PROPERTY		
			WATER	DETERGENT SOLUTION	LIGHT
A	Cotton	Light pink	Moderate	moderate	Moderate
A	Satin (synthetic)	Orange	Good	good	Good
A	Paper	Stained pink	-	-	Moderate
B	Cotton	Bright yellow	Good	good	good
B	Satin (synthetic)	Bright yellow	Good	good	good
B	Paper	Yellow	-	-	good

RESULT AND DISCUSSION

The Extract and their Solvents

Trial extraction showed that water did not extract significant colouring matter from sample A; but is produced yellowish emulsion from sample B; alcohols and benzene were found to produce deeply coloured extracts both in the cold and in the hot solvents. However, because of the intended applications athanol (local gin) was found most suitable for sample A, methanol for sample B.

Extraction of sample A with (Local gin) using soxhlet apparatus gave a yield of 8.5% orang-reddish dye and extraction of sample B with methanol using the same apparatus yielded 12.1% wine-red dye which turned yellow on dilution. Therefore local gin (crude ethanol) and methanol are recommended for industrial extraction of the dyes from sample A and sample B respectively.

Characteristics of The Plant Dyes

The UV absorbance of 1% (W/V) solution of the extracts in ethanol and methanol respectively showed that Extract A dye absorbed maximally between 500 and 575nm while extract B had infinite absorbance from 700nm. The UV absorption characteristics showed the –

OH of the phenol and the –OH of carboxylic acid band (3700 – 3100 cm^{-1}). – CH_3 and – CH_2 stretch (3000-2800cm^{-1}); the –C = C –H of aromatic compounds (3090 – 3070 cm^{-1}), the C = 0 of the carboxylic acid, aldehydes, and 6 → membered ring Ketone (saturated and unsaturated) (1780 – 1500 cm^1).

The presence of these functional groups were confirmed by chemical tests in which:

- the ethanolic solution extracts formed violet colour with Iron III Chloride indicating presence of phenolic compound;

- the ethanolic solution extracted formed white precipitate with 2,4 – dinitrophenylhydrazine indicating presence of carbonyl group (C = 0) and Tollen's test showed that the carbonyl group was of the aldohyde functional group;

- the extract formed purple solution with aqueous sodium hydroxide solution showing that the extracts contain hydroxyanthraquinone compound;

- the extracts decolourized bromine water indicating unsaturation in the system (Vogel, 1968).

With above results the extracts could contain dyes of the anthraquinone class shown in Fig. I.

Fig. I Suggested Structure of the Plant Dye (Anthraquinone Dye) X, Y, Z, being substituents some of which are auxochromes (Abrahart, **1977**).

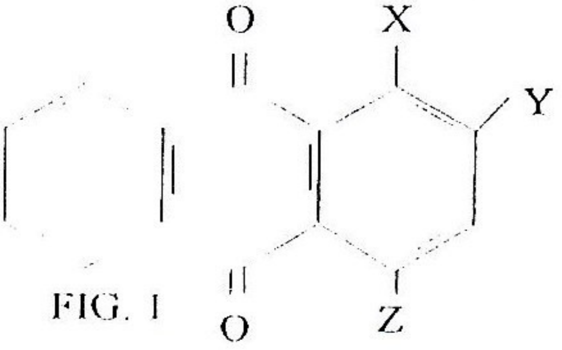

FIG. I

The Dyes as Colour Indicator in Acid/Base Medium

Each alcoholic solution of the dye extract exhibited different colours in acid and base solutions. Extract A was orange in acid (0.1MHCL) and red in the alkaline (0.1MNaOH) solution. Extract B solution turned acid solution orange while it coloured an alkaline solution yellow.

Dye Extracts As Colour Indicator In Ph Titration Of Strong Acid Against Strong Base

In titrating above solutions with the dye extracts, extract B indicated a sharp colour change at the end point, changing from yellow in the alkaline solution to orange when a little excess of the acid was added to the base: extract A did not show a sharp end point. The average titre obtained was 10.95cm^3 (0.1MHCL) for 10cm^3 of approximately 0.1MNaOH solution giving the actual concentration of the base as 0.1095M (0.11M). this compared well with 11.0cm^3 (0.1MHCL) obtained with standard methyl orange indicator, which gave concentration of the base also as 0.11M. also graphs of pH against volume when extract B and methyl orange were used as indicators separately, gave the end point as 11.0cm^3 of the acid. The results are shown in Fig. 1.

Plant Dyes As Fabric And Paper Dyes

Table 3 shows the colour and the fastness properties of the dye-extracts on fabrics and paper. Extract A dyed satin (synthetic fabric) with orange colour and had good fastness properties in water, washing (detergent) solutions and when exposed to daylight. Although it also dyed cotton fabric, the fastness properties were not as good as these of the synthetic (satin) fabric.

Extract B dyed cotton and satin bright yellow and showed good fastness property to water, detergent solutions and daylight.

Extract A only stained paper pink while extract B dyed paper yellow and showed good fastness property when exposed to daylight.

CONCLUSION

Local gin was found suitable for extracting the orange coloured dye from sample A (Sterculia tragacantha seeds) while methanol extracted a high yield of wine-red dye from sample B (Zingiber officinale rhizome) IR and UV absorption characteristics and chemical analysis showed that these plant dyes belong to the anthraquinone dye class.

The dye from sample A was found useful in dyeing white satin (synthetic) fabric orange while sample B extract dyed natural (cotton) fabric, paper and synthetic (satin) fabric bright yellow in solvent systems. Sample B dye extract was also suitable as an indicator in the pH titration of a strong acid against a strong base, hence it can be used as a substitute for the standard colour indicators in such pH titration.

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FIG 2: GRAPH OF pH AGAINST VOLUME OF ACID (0.1MHCl)