British Journal of Applied Science & Technology
4(20): 2921-2930, 2014

SCIENCEDOMAIN *international*
www.sciencedomain.org

Extraction and Utilization of Natural Dyestuffs from the Bark of Whistling Pine and the Root of African Peach

E. Osabohien[1*] and J. O. Otutu[1]

[1]Department of Chemistry, Delta State University, P.M.B 1, Abraka, Nigeria.

Authors' contributions

This work was carried out in collaboration between both authors. Author EO designed the study, conducted the experimental work, wrote the protocol and the first draft of the manuscript. Author JOO assessed the dye plants and made some technical inputs into the work. Both authors read and approved the final manuscript.

Original Research Article

Received 20th December 2013
Accepted 23rd March 2014
Published 24th May 2014

ABSTRACT

Aims: This work is aimed at assessing the dye and colouring potentials of the extracts from the bark of whistling pine and the root of African peach. It is intended to apply these extracts for textile dyeings, drink and food colourings.
Place and Duration of Study: The study was carried out in the Department of Chemistry, Delta State University, Abraka, Nigeria, between October, 2012 and March, 2013.
Methodology: The bark of the plant, whistling pine (*Casuarina equisetifolia*) and the root of African Peach (*Nauclea latifolia*) were collected, chopped, dried and pulverized. The dye extracts were obtained using ethanol (absolute) as extracting solvent. The crude dye extracts were recrystallized in carbon tetrachloride (CCl_4) for purification. The percentage yields, melting points, pH and R_f values, UV/visible absorptions and IR spectra were determined. Textile (cotton) dyeings, wash and light fastness tests, drink (local gin) and food (pap) colourings were performed.
Results: Whistling pine bark yielded reddish brown colour while the root of African peach yielded brown colour. They gave respectively 13.67% and 9.26% yield, pH values of 5.93 and 5.67, M.pt. of 194ºC and 210ºC, R_f values of 0.84 and 0.64. The dyeings showed varied colour shades, poor wash and light fastness on cotton fabrics.
Conclusion: The two dye plants produced fine colours on textile, food and drink. The poor wash and light fastness of dyed fabrics improved with mordanting.

**Corresponding author: E-mail: osabohieneemma@yahoo.com;*

Keywords: Natural dyes; textile dyeing; food and drink colouring.

1. INTRODUCTION

Dyes are chemical substances used to impart colours to substrates such as cosmetics, foods, drugs, hairs, furs, textiles and polymers [1-3]. All dyes were basically natural, extracted from some plants and animals until the advent of synthetic dyes in the middle of 19^{th} century. The roots, stems, leaves, flowers and fruits of various plants supplied vegetable dyes. Certain mollusks found on the shores of the Mediterranean Sea supplied animal dye as the famous tryrian purple [2,4-5].

Despite the teething problems associated with the use of natural dyes such as poor yield, poor affinity for textile materials and may be pollution hazards, there is the need for sustainable processes which can be seen as the driving force for the development of new strategies to the return of natural dyes. Natural dyes can exhibit better biodegradability and generally have higher compatibility with the environment compared to synthetic dyes [6-12].

Furthermore, there have been worldwide efforts to promote the cultivation of natural dye plants and their application for dyeing by some projects such as the Pris CA of Italy and INDINK in UK [12,13]. There is the re-evaluation of ecology as a major trend for influencing colour, and it is believed that naturally dyed fabrics can meet the current global greening movement [14]. Nigeria has abundant natural resources in terms of dye plants which stores dyes in parts such as the roots, barks, leaves, seeds, fruits and flowers. Most of these plants have both medicinal and dye potentials [11,15-17].

Casuarina is a genus of 17 species in the family *casuarinaceae*, native to Australasia, the Indian subcontinent, Southeast Asia and Islands of the western Pacific Ocean. They are evergreen shrubs and trees growing to 35m tall. The foliage consists of slender, much-branched green to grey-green twigs bearing minute scale-leaves in whorls of 5–20. The flowers are produced in small catkin-like inflorescences and are simple spikes. The fruit is a woody, oval structure superficially resembling a conifer cone made up of numerous carpels each containing a single seed with a wing. The species are food source for the larvae of hepialid moths. *Casuarina equisetifolia L.* also called Australian pine, Beach Sheoak and common ironwood is a common tropical seashore tree known as common ironwood, Beefwood, Bull-oak, or whistling-pine. It is often planted as a windbreak. The wood of this tree is used for shingles, fencing, and is said to make excellent, hot burning firewood. The tree has delicate, slender ultimate branches and leaves that are no more than scales making the tree look more like a wispy conifer. It is widespread in the Hawaiian Islands and also an introduced, invasive plant in Bermuda [18].

Nauclea latifolia commonly called African peach is a plant belonging to the family, *Rubiaceae*. It is called “Epe” by the Isokos of Delta State, Nigeria, and it is mainly used for medicinal purposes. It is a straggling shrub or small tree native to tropical Africa and Asia. It is reported to be used in the treatment of malaria, gastrointestinal tract disorders, sleeping sickness, prolonged menstrual flow and hypertension. Different parts of the plants are commonly prescribed traditionally as remedy for diabetes mellitus [19]. The roots are used as an aphrodisiac, analgesic and remedy for sexual asthenia (loss of strength) in the Congo and used as tonic or stimulant or restorative agent in Guinea, West Africa. The bark of the stem is used as an aphrodisiac in Nigeria.

This research work is based on assessing the dye and colouring potentials of the extracts from the plants, whistling pine and African peach. The work is intended to utilize the extracts to dye textile (cotton) fabrics, colour local gin known commonly as ogogoro and pap also called akamu.

2. MATERIALS AND METHODS

2.1 Materials

The bark of whistling pine *(Casuarina equisetifolia)* and the root of African Peach *(Nauclea latifolia)* were obtained from the premises of Delta State University, Abraka and Ozoro market respectively, the cotton fabrics, local gin and pap were bought from Abraka market, all in Delta state, Nigeria. Industrial, analar grades and BDH chemicals and equipment used for this work were got from the chemical laboratory, Department of Chemistry, Delta State University, Abraka, Nigeria.

The UV/visible spectrophotometer used was obtained from Global Environmental consultants, Warri, Delta State, Nigeria while the infra-red spectrophotomer was obtained from Nigerian Institute of Science Laboratory Technology, Ibadan, Nigeria. The Gallen kemp melting point apparatus was used to determine melting points of the solid dye extracts.

2.2 Methods

2.2.1 Solvent extraction

The bark of the whistling pine and root of the African peach respectively were collected, chopped, dried and ground to fine powder to allow for most intimate contact with solvent [20]. Measured quantities of pulverized samples were fed into the soxhlet extractor and mixed with the absolute ethanol as solvent in a ratio of 1:50 of powdered plant sample to ethanol solvent. The mixture of solvent-sample was refluxed for 3h. The extract phases generated through several operations of the extraction process were first distilled to recover parts of the solvent before evaporating to dryness to obtain dried solid dye samples. The crude extracts were recrystallized using carbon tetrachloride as solvent and finally air dried to obtain purified dye samples. The following characteristics; percentage yield, pH value, melting point, colour and solubility parameters were determined for the purified dye samples.

2.2.2 Thin-Layer Chromatography (TLC)

The eluting solvents in the TLC operation were Diethyl ether, glacial acetic acid and toluene in a ratio of 3:4:3 respectively. The dye spots on the chromatoplate were eluted with solvent mixture in a covered beaker. The chromatograms were developed on a microscope slide [21]. The colour spots were scraped off the plate, dried and visually observed for identification of actual colours.

2.2.3 UV/Visible and Infra-red spectrophotometry

The UV/visible spectra of the dye specimens were recorded with the Pye unicam 5625 UV/visible spectrophotometer. The absorption peaks (λ_{max}) at different absorbances were obtained using hexane as solvent to make the dye solutions. The infra-red spectra was determined by the use of BS instrument (Figs. 1 and 2).

2.2.4 Dyeing process of the textile fabrics

2.2.4.1 Preparation of the dye baths and dyeing

1.0g each of the dried dye samples were measured into two separate beakers and made into paste forms with little water. They were then washed into two separate clean 500ml flat-bottom flasks with water to make up to 100ml dye solutions. The solutions were boiled for about 5 min. to aid good dissolution of the dyes and then cooled. For a liquor ratio of 50:1, 2.0g of scoured white cotton material was introduced into the dye bath and heated to about 70ºC and left for about 30 min. to achieve optimum exhaustion of the dyebath. The materials (cotton) from each dye bath were removed and allowed to cool. They were then rinsed with cold water to remove loose dye particles adhering to the fabric surfaces. The cotton fabrics were then air-dried and tested for light and wash fastness properties.

In another operation, scoured white cotton fabrics were mordanted with 2% solutions of potassium dichromate, alum iron sulphate and stannous chloride respectively and warmed for about 30 min. at about 60ºC. They were then dyed in a similar way in the dyebaths of the two different dyestuffs used. The mordanted and unmordanted fabrics were compared in terms of colour shades, hues and fastness properties (Table 4).

2.2.5 Fastness properties of dyed fabrics

2.2.5.1 Light fastness

Two sets of the dyed cotton fabrics were prepared. One set was exposed to sunlight for a period of about a week, while the second set was kept in the dark wrapped in black polythene bags. The exposed ones were rated to the unexposed fabrics on a grey scale [5,11,21-23]. This was done in the absence of the American Association of Textile Chemists and Colourists (AATCC) standards.

2.2.6 Wash Fastness

Here, also two sets of the dyed cotton fabrics were prepared. One set was washed with soap solutions at room temperature for 30 min. in a lini test wash wheel machine in accordance with ISO washing test No. 3. The washed fabrics were compared with the unwashed fabrics in a grey scale [12,17,23].

2.2.7 Food (pap) colouring

10.0g of pap (akamu) was first dissolved in water to make the pap solution. Then 1.0g of dry dye sample was measured into a glass beaker, water was added gradually with stirring to make about 100ml dye solution and then heated to boil. The boiling dye solution was poured into the pap solution in a cooking stainless pot and stirred vigorously until a uniform semi-solid pap meal was obtained.

2.2.8 Alcoholic drink (illicit gin) colouring

1.0g of the dry dye sample was mixed with 100ml of illicit gin commonly called ogogoro in a glass bottle. The bottle was corked and shaken vigorously for about 10 min. A homogenous mixture was formed with fine colour shades respectively for the two different dye samples under test.

3. RESULTS AND DISCUSSION

The dye samples derived from the bark of whistling pine and root of African peach were found to be soluble in hot water and organic solvents. The yields were however poor (Table 1) which is characteristic of natural dyes [5,11]. Both dyes were found to be acidic with pH values of 5.93 and 5.67 respectively (Table 1). The bark of the whistling pine produced a reddish brown colour with melting point of 194ºC while the root of the African peach gave a brown colour with melting point of 210ºC. The chromatograms of the dye samples from the whistling pine and African peach were evaluated which gave R_f values of 0.84 and 0.64 respectively (Table 2). From Table 3, the absorptions of the dye samples at λ_{max}. 650-750nm are consistent with reddish-brown colours of the dyes [24-25]. In Fig. 1, the 1R absorptions of the dye showed the presence of – OH and NH_2 groups in the 3950-3200cm^{-1} regions. This may be due to presence of alcohols, phenols, amines and amides. Also, C-H stretching vibrations were observed at the 2974cm^{-1} region. The C-H bending vibrations in the region of 1456.78cm^{-1} band is associated with hydrogen bonded to SP^3 hybridized carbons. Absorptions also exist in the regions of 1760-1690 cm^{-1} for the C=O group which may be due to the presence of carboxylic acids. The absorption at 1653.78cm^{-1} may be due to the presence of ethers (C-O-C) bonds. The absorptions at 1089.29-1049.50cm^{-1} and 880.56cm^{-1} regions may indicate the presence of sulphur related compounds and C-O group of alcohols and esters [11]. In Fig. 2, the same groups as in Fig. 1 were present such as the OH, C-H str, C-H str. in plane bend, C-O and S. There exist a broad band between 800-500 cm^{-1} regions, this may be presence of benzene ring (quinone) structure in both dye samples. The absorption spectra did show the presence of impurities which may have arisen from incomplete removal of impurities through the recrystallization processes.

Table 1. Physical properties of dye extracts

Dye plant	Yield (%)	pH value	M.pt (ºC)	Colour of aqueous solution	Solubility	
					Cold water	Hot water
Whistling pine	13.67	5.93	194	Reddish brown	Sparingly soluble	Soluble
African peach	9.26	5.67	210	Brown	Sparingly soluble	Soluble

In Table 4, the dyed cotton fabrics showed varied colour shades and hues with different mordants, $K_2Cr_2O_7$, $SnCl_2$, $FeSO_4$ and alum. The mordanted fabrics showed better light and wash fastness properties compared to the unmordanted fabrics. The dye derived from the bark of whistling pine showed better light and wash fastness properties compared to that obtained from the African peach (Table 4). This may be due to the higher yield and tinting strength [5,11,12,17,26].

Table 2. Evaluation of Chromatograms

Dye extract	Distance moved by solvent front (cm)	Distance moved by solute (cm)	R_f value
Whistling pine	6.7	5.6	0.84
African peach	7.0	4.5	0.64

Table 3. UV/visible spectral analysis

Dye extract	Absorbance	λ_{max} (nm)	Structure assignment
Whistling pine	1.529	650	Quinone type
	1.481	750	Structure suspected,
	1.331	850	Chromophoric systems
	0.982	950	present
African peach	2.390	650	Quinone type
	2.297	750	Structure suspected,
	2.204	850	Chromophoric groups
	2.050	950	present

Table 4. Colour shades/hues and fastness properties of dyes

Dye extract and mordants	Fabric colour (cotton)	Light fastness (Gray scale)	Wash fastness
Whistling Pine			
Unmordanted	Lilac	3-4	3-4
$K_2Cr_2O_7$ mordant	Light brown	4-5	4-5
$Sncl_2$ mordant	Light brown	3-4	4-5
$FeSO_4$ mordant	Black	4-5	4-5
Alum mordant	Lilac	3-4	4-5
African Peach			
Unmordanted	Light brown	2-3	2-3
$K_2Cr_2O_7$ mordant	Creamish yellow	3-4	3-4
$SnCl_2$ mordant	Light yellow	2-3	2-3
$Feso_4$ mordant	Light brown	3-4	3-4
Alum mordant	Light yellow	2-3	2-3

Key: 1-2 most colour change; 2-3 colour change; 3-4 slight colour change; 4-5 colour retained

Table 5 shows the different colour hues imparted on food such as pap (akamu) and illicit gin (ogogoro). The colours improved the facial values of these food and drink. The harmless nature of most of these natural dyestuffs could allow for these applications since most of their sources have food and medicinal values [7,19,27].

Table 5. Colour imparted on substrates

Dye extract	Substrate	Colour imparted
Whistling pine	Pap (akamu)	Light brown
African peach	Illicit gin (ogogoro)	Reddish brown
	Pap (akamu)	Light yellow
	Illicit gin (ogogoro)	Brownish yellow

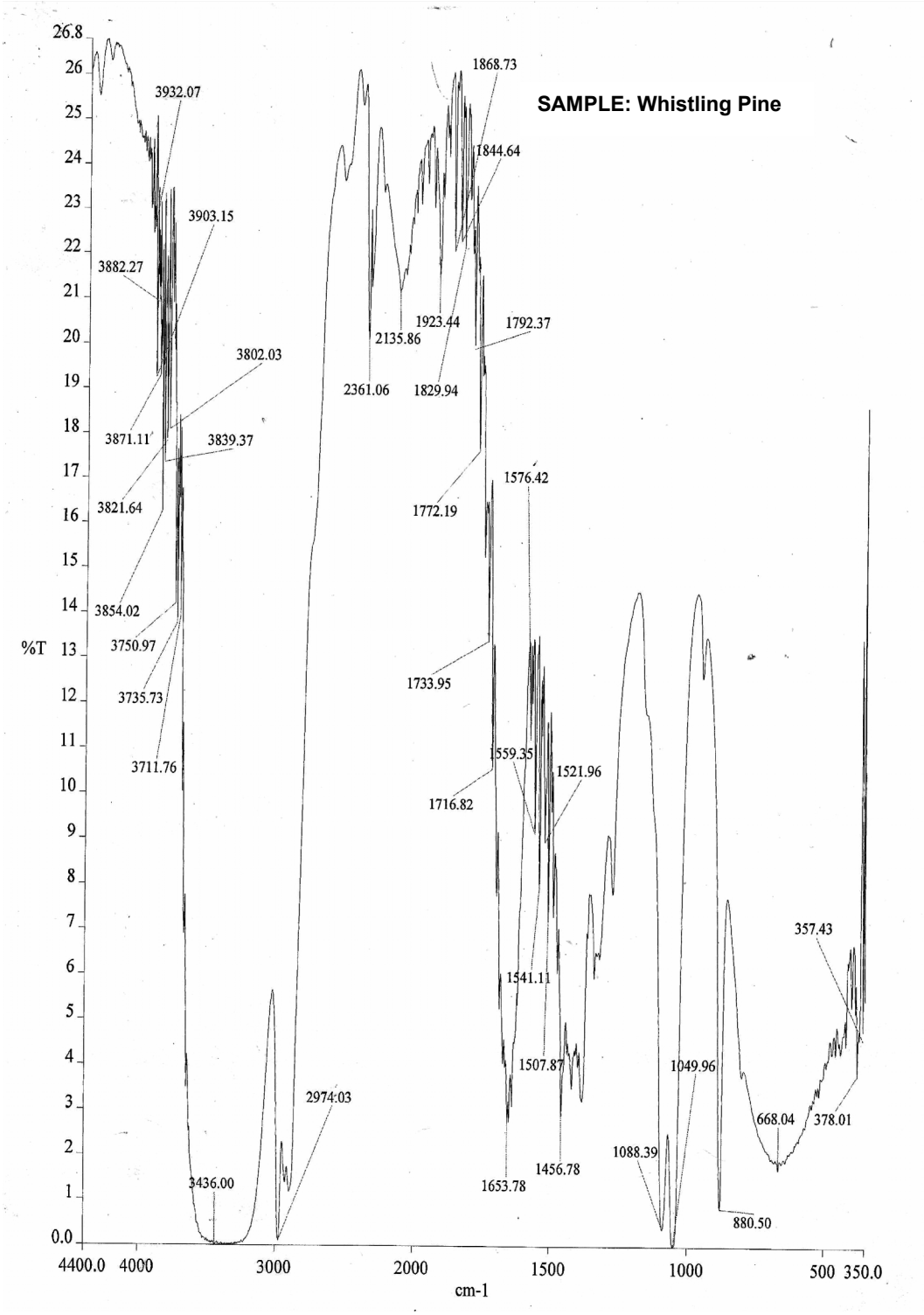

Fig. 1. IR Spectra of dye extract from Whistling Pine

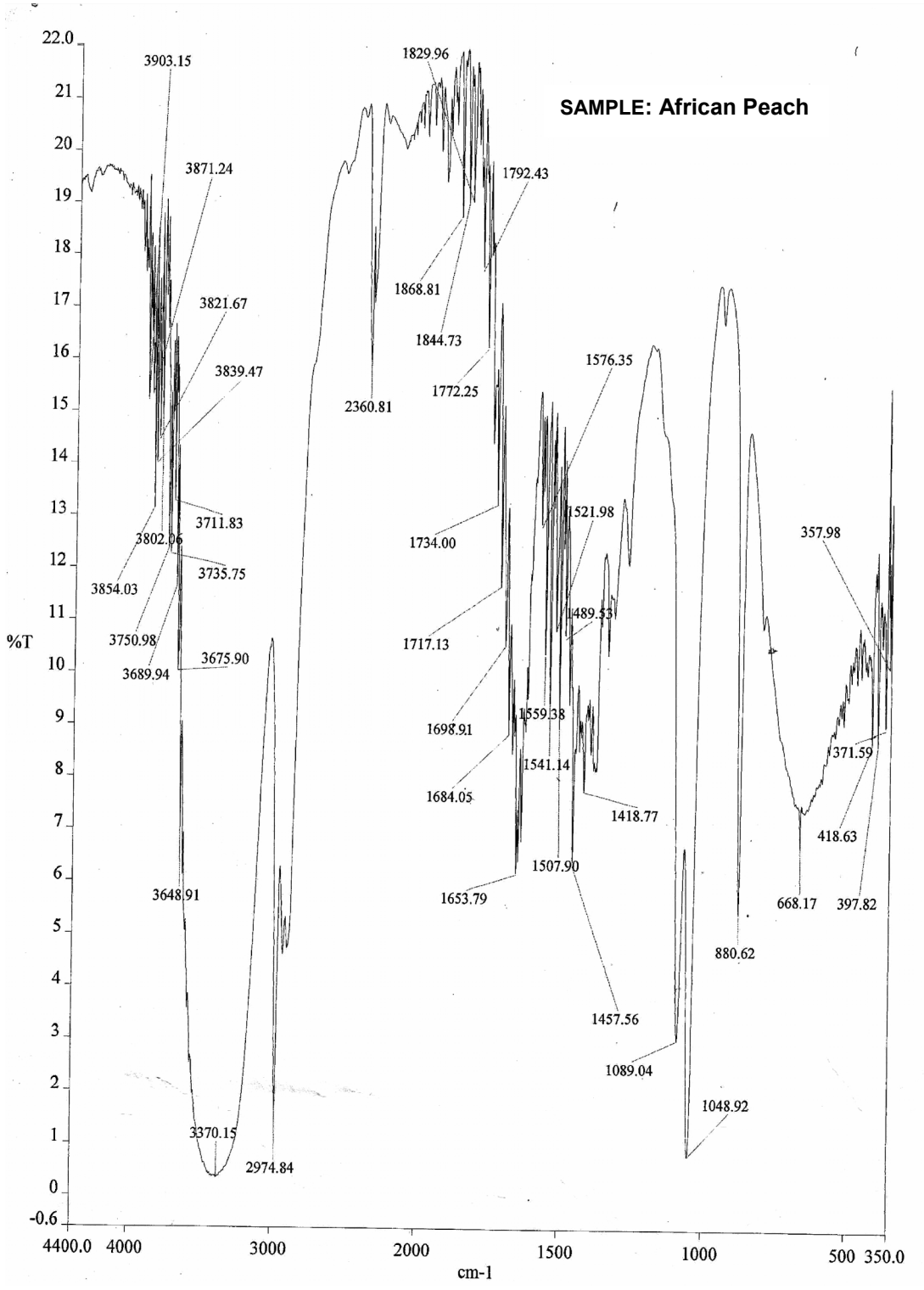

Fig. 2. IR Spectra of the dye extract from African Peach

4. CONCLUSION

This work has achieved some level of success in the use of locally sourced materials for dye applications in textiles, food and drink colourings. However, the use of mordants in textile dyeings was found to be essential in improving colour shades and fastness properties of the dyes. Both plants, the whistling pine and African peach have been found to be useful as wind break and medicine respectively. It is in this light that these plant dyestuffs are recommended for textile dyeing and colouration of foods, drinks and even cosmetics for the consumption of man. The use of these locally available raw materials that are renewable for our textile, food and cosmetics industries would enhance their value and increase national resource development and gross domestic products.

COMPETING INTERESTS

Authors declare that there are no competing interests.

REFERENCES

1. McGraw-Hill, Encyclopaedia of Science and Technology. 6th ed. New York: McGraw-Hill Books Co.; 1970.
2. Giles GH. A Laboratory course in Dyeing. 3rd ed. Bradford: The Society of Dyers and Colourists; 1974.
3. Kirk-Othmer. Encyclopaedia of Chemical Technology. USA: John Wiley and Sons; 1976.
4. The New Encyclopaedia Britannica. London: RP Gwin and Co.; 1974.
5. Osabohien E, Ukponmwan DO. Extraction of natural dyes from some local plants. J. Chem. Soc. Nigeria. 2002;27(2):139-142.
6. Spanier E, Karman N. The Royal Purple and Biblical Blue, Argaman and Tekhelet ed., Jerusalem Keter; 1987.
7. Gill D. The Return of Natural dyes. J. Soc. Dyers and Colourists. 1993;109:32.
8. Brian G, Jeffrey HP. Dyeing with vegetable dyes. J. Soc. Dyers and Colourists. 1993;109:5-7.
9. Paul S, Glover E, Sharma A. Eco-friendly dyeing of wool with Jatropha dye. Int. Dyer. 2003;188:55-60.
10. Guinot P, Roge A, Gargadennec A. Andry C. Dye plants screening: An approach to combine past heritage and present development, Coloration Technol. 2006;122:93-101.
11. Osabohien E. Extraction and utilization of natural dyestuffs from *Maesobotyra staudtii* and *Chrosophyllum albidum.* Nig. J. Sci. and Environ. 2009; 8:93-97
12. Otutu JO, Osabohien E, Efurhievwe EM. Extraction of natural dyes for textile dyeing from the by-products of the timber industry. Biosci. Biotechnol. Res. Asia. 2010;7(1):87-92
13. Tsatsaromi E, Liakopoulou-Kyriakides M. Effects of enzymatic treatment on the dyeing of cotton and wool fibres with natural dyes. Dyes and Pigments. 1995;29(3):203-209.
14. Eunjou Y, Ju-Yeon C. Colour analysis of natural-dyed fabrics. Wiley Periodicals. 2008;33:2.
15. Keay RWJ. Trees of Nigeria. New York: Clarendon Press, Oxford; 1989.
16. Gill LS. Ethnomedical uses of plants in Nigeria. Benin-City, Nigeria: University of Benin Press; 1992.

17. Akpuaka MU, Chuwuneke C, Agho G. The Dyeing of textile fabrics with natural dyes from some local trees. J. Chem. Soc. Nigeria. 1998;23:47-52.
18. Wikipedia. The Free Encyclopaedia, Casuarina. Accessed 10 October, 2013. Available: en.wikipedia.org/wiki/casuarina.
19. Abubakar GD, Ameh AS, Atawodi E, Sani I. Effects of ethanol extract of the leaves of *Nauclea latifolia* on diabetes mellitus in caemic and streptozotocin-diabetic rats. African J. Trad. Compliment Altern. Med. 2008;5:201.
20. Stahl E. Thin-layer Chromatography: A laboratory handbook. London: Academy Press; 1965.
21. Vogel AI. Textbook of Quantitative Inorganic Analysis. 4th ed. London: Longman; 1978.
22. Trotman ER. Dyeing and Chemical Technology of textile fibres. 4th ed. London: Charles Griffin; 1970.
23. Nkeonye PO. Fundamental principles of textile dyeing, printing and finishing. Zaria: Ahmadu Bello University Press; 1987.
24. Fessenden RJ, Fessenden SJ. Organic Chemistry. 4th ed. California: Brooks/Cole Pub. Co.; 1990.
25. Anonymous. Chemistry of Dyes: Basis of colour. Webprojects. 2002. Accessed 5 September; 2013. Available: price/colour.htm.
26. Otutu JO, Ukponmwan DO, Oviawe AP. Synthesis and fastness properties of Disazo disperse dyes derived from 4-aminophenol for synthetic polymer fibres. J. Chem. Soc. Nigeria. 2007;32(2);65–71.
27. Osabohien E, Otutu JO, Ukponmwan DO. Dyeing and colouring using the extract from a plant; *Bosqueia angolensis*. Inter. Jour. Scientific Res. 2013;3(1):1-6.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history.php?iid=537&id=5&aid=4682