JORMAR 2(1), 2005, 39-47 ISSN: 1597-3204

Synthesis of Azo dyes from the fruit husk of *Parkia clappertoniana*

*[1]Putshaka, J. D., [2]Harami, A. and [3]Zakari, L.

1. *Department of Leather Technology, Federal College of Chemical and Leather Technology, P. M. B. 1034, Samaru, Zaria, Nigeria.*
2. *Chemistry Programme, Abubakar Tafawa Balewa University, P. M. B. 0248, Bauchi, Nigeria*
3. *National Research Institute for Chemical Technology, P.M.B.1052, Zaria, Nigeria*

Abstract

The synthesis of an azo dye by coupling the water extract of the fruit husk of Parkia clappertoniana, a polyphenolic compound with diazonium salt was attempted. A yellow dye soluble in water was obtained. The dye was characterized using spectroscopic methods (infrared and ultraviolet) and chromatographic analysis. Results obtained showed the synthesized dye to have similar properties, which are characteristic of conventional azo dyes. It is therefore deducted from these findings that C. clappertoniana can serve as an alternative source of raw materials for Azo dye production.

Introduction

Dyes are coloured natural or synthetic organic compounds possessing properties of imparting colours on other materials or substances. When applied on these materials such as fibres, a dye must not only be capable of attaching itself to the material(s), but must also retain its colour on prolonged exposure to light, water and soap among others. This property is often referred to as the fastness property of the dye [1].

Before the advent of synthetic dyes, natural colouring substances have been used in dyeing of fabric and other materials. With the growth and development of the dye industry, many dyes have been prepared by various methods using aromatic hydrocarbons; benzene, toluene, naphthalene, anthracene, pyrene as raw materials [2].

Of the many methods used in the synthesis of azo dyes, the commonest is by diazonium coupling [3]. Phenols are known to couple in the para- position with diazonium salts in alkaline solution to form hydroxyazo compounds [4,5].

A new trend is being pursued by various dye manufacturers to produce dyes by coupling diazo compounds with tanning condensation products. Dyes based on phenolic syntans, resorcinol resins and condensation products of phenols are at various stages of development in the dye industry [6].

A recent study on the application of modified extract produced by coupling *Lawsonia inermis* with diazotized primary amine have shown that the dye produced was found to dye chromme tanned leathers with different shades of brown [7].

Parkia clappertononiana also referred to as *Parkia filicodea/oliveri* is grown throughout the climatic zones of Nigeria [8]. Phytochemical studies (isolation, identification and characterization) of the fruit husk of *Parkia* revealed

*Corresponding author

that it contained about 45% tannin content of the condensed type [9].

In this study, an alternative method of synthesizing azo dyes using a condensed tannin which can substitute β–naphthol is reported. It can also be used in the event of any short fall in the availability of synthetic products used in the manufacture of synthetic azo and azoic dyes.

Materials and Methods

Collection and preparation of sample

The fruit pod of the plant was collected from Basawa village in Sabon-gari local government area of Kaduna State, Nigeria. The husk was separated from its seed and yellow pulp. It was then dried in the sun and subsequently oven dried at 60^0C. After adequate drying, the husk was pulverized in a wooden mortar with a pestle. The powdered sample was sieved through a woven wire mesh of 0.5mm.

Extraction

50g of the sample were defatted with n-hexane by using a soxhlet extractor for 8 hrs yielding a yellow oily substance. Extraction of the sample was carried out with distilled water using a Procter extractor. A brown extract was obtained which was concentrated by heating on a hot plate at 60°C to a low volume of about 50mls and dried in an oven at about 60°C. 28.9gram (57.8% yield) of the dried extract was obtained and kept in a sample bottle for further analysis.

Preparation of Diazonium salt

Benzene diazonium chloride which is the reagent used in the coupling reaction was prepared by the slow addition of $2.5cm^3$ phenylamine to $15cm^3$ of concentrated hydrochloric acid in an ice bath in a fume cupboard. A solution of 4.5g sodium nitrite ($NaNO_2$) in $15cm^3$ distilled water was prepared and cooled in a refrigerator out of which $7.5cm^3$ of the cold sodium nitrite was taken and slowly added to the mixture (of phenylamine and hydrochloric acid) in a fume cup-board with constant stirring in an ice bath. After complete addition, the reaction mixture was tested with starch iodide paper to ensure the completion of the diazotization process.

Diazonium coupling reaction

About 5g of the extract of the sample was dissolved in $30cm^3$ of distilled water and made alkaline with $50cm^3$ of 20% NaOH. This was cooled in an ice-bath for 30mins. The benzene diazonium chloride was slowly added to the alkaline solution of the extract in small portions in an ice-bath (in fume cupboard) with constant stirring until all of it was added.

After the reaction, the coupled extract (*Parkia* dye) was filtered and dried at 60°C in an oven. This temperature was maintained to avoid denaturing the product. After drying the dye was milled into powder and the melting point of the dye determined using the electro-thermal melting point apparatus. The sample decomposed at 220°C.

A commercial dye (acid dye), which is commonly used for dyeing in the leather industry served as a reference sample in spectroscopic and chromatographic analyses. The dye decomposed at 240°C.

Spectroscopic analysis

The infrared spectra of both the *Parkia* extract and coupled *Parkia* extract (*Parkia* dye) were obtained in Nujol mull using ATI Mattison Genesis FTIR Spectrometer at the laboratory of National Research Institute for Chemical Technology, Zaria, Nigeria. The major bands were observed as shown in Figures I, 2 and 3 for Parkia extract and coupled Parkia extract and the reference sample respectively.

The ultra-violet spectroscopy of the *Parkia* extract and the *Parkia* dye samples were carried out using CECIL CE 304D spectrophotometer at the Chemistry laboratory of the Abubakar Tafawa Balewa University, Bauchi. The wavelength of maximum absorption (λ max) of the *Parkia*

extract and coupled Parkia extract is shown in Figure 4. The result of both samples were recorded in nanometers (nm)

Chromatographic analysis

The various components of *Parkia* extract, the coupled Parkia extract and that of the reference sample were separated by thin layer chromatography. This was carried out using already prepared chromatographic plate coated with silica gel with dimension 20 x 20 cm. The spots or chromatogram were developed by the ascending technique using butan-1-ol: ethanol: 0.2M ammonia in the ratio (3:1:1%).

Results and Discussion

Infrared spectroscopy

The infrared spectroscopy of *Parkia extract*, coupled *Parkia* extract (*Parkia* dye) and that of the reference sample (conventional dye) indicating absorption bands are shown in Figures 1, 2 and 3 respectively.

The result of infrared analysis of *Parkia* extract in figure I, shows that there is an O-H stretch characteristic of phenols. This is indicated by the broad absorption band at 2853.73cm^{-1} The sharp and intense band at about 2940cm^{-1} and 28853.73cm^{-1} are as a result of C-H stretching vibrations. The bands at 1692.63cm and 1605.71 cm are due to C=C stretch in aromatic nuclei [10]. C = C stretching vibration can be seen at 1406.75cm^{-1} and 1377.18cm^{-1}. The band showing at 1203.42cm^{-1} and 1031.23cm^{-1} are as a result of C-O stretching vibrations in aromatic compounds.

Fig. 2 is the infra-red spectrum of *Parkia* dye. The broad bands of 3357.92 and 3196.12cm^{-1} are due to O-H stretch in the dye. The intense absorption band at about 2945.00 and 2953.60cm^{-1} and the weak bands at 2725.13cm^{-1} are as a result of C-H stretch. The sharp band at 2358.48 is due to C =N band stretch while the broad absorption band at 1628.86cm^{-1} is as a result of aromatic C = C stretch. The intense bands at 1461.37 and 1376.79cm^{-1} are absorption band due to C – H stretching vibration. C-H bending is observed as an absorption band at 1304.41cm^{-1}. C-O stretch is characterized by the absorption bands at 1153.74cm^{-1}, and 1031.28cm^{-1}.

The infrared spectrum in figure 3 is the spectrum of the conventional acid dye used as the reference sample in this study. The absorption band at 3367.61cm^{-1} indicates an O-H stretch. The bands at about 2940.00cm^{-1} and 2853.36cm^{-1}are C-H stretch. The weak absorption band at 2688.76cm^{-1} is also as a result of C-H stretch.

A nitrile absorption band can be seen by the sharp band at 2367.58^{-1} . The fairly broad absorption band at 1568.23cm^{-1} is an aromatic C=C stretch. The sharp and intense band at 1460.41 and 1376.70cm^{-1} are due to C-H stretching vibration. The band at 1158.48cm^{-1}, 1103.68 and 1038.36cm^{-1} are as a result C-O stretch. C-H out of plane deformation is shown in the rest of the band in the finger print region.

It must however be noted that the azo (-N=N-) stretching vibration is inactive or cannot be detected in the infrared spectral region, but appears at 1550 – 1650cm^{-1} in the Raman spectra.

Ultra Violet Spectroscopy

Figures 4 (A and B) show ultra violet spectra indicating the wavelength of maximum absorption (λ_{max}) of the *Parkia* extract and *Parkia* dye respectively.

The results show that the extract (figure IV a) has a wavelength of maximum absorption at 203nm, 275.5nm and a weak absorption at 370.0nm with absorbance at 1.150, 0.517 and 0.046 respectively, while the λ_{max} for the coupled *Parkia* dye (figure 4 b) are at 238.5 and 370.0 with absorbance at 0.418 and 0.116 respectively. From this results it can be deduced that the λ_{max} 203 in the extract is as a result, n-π^* transition in chromophores which may occur within the uv region of 200 –

205 as in aromatic compounds [11]. The weak absorbance of the *Parkia* dye when compared with that of the *Parkia* extract indicate that much of the colour of the dye was reflected and little absorped.

The λ_{max} 275.5nm in the *Parkia* extract is close to the λ_{max} characteristic of catechol with λ_{max} 278nm, compounds such as resorcinol with λ_{max} 277nm and naphthalene with λ_{max} 275nm. The region of absorption at λ_{max} 238.5 in the *Parkia* dye closely correspond to λ_{max} of compounds such as nitroaniline (λ_{max} 235), thiophene (λ_{max} 235). The λ_{max} 370nm in both the *Parkia* extract and *Parkia* dye is closely related to the λ_{max} of compounds like anthracene (λ_{max} 375nm), m-nitro aniline (λ_{max} 373nm).

Chromatographic analysis

The result of the chromotographic analysis carried out can be seen in figure 5 indicating the retention factor (R_f values) for the components of each of the samples i.e. *Parkia* extract, coupled *Parkia* extract (*Parkia* dye) and the reference sample.

From the chromatogram it can be deduced that the gray – green spot agrees with the R_f value of the *Parkia* extract (R_f 0.56) within the range of the R_f values of 0.5 – 0.58 typical of catechols [12]. There are four spots indicated on the result of the *Parkia* dye with R_f values of 0.28, 0.39, 0.53 and 0.86. While that of the reference sample shows that there were five different spots with R_f values of 0.30, 0.46, 0.55, 0.64 and 0.86 respectively. From the result obtained, it can be observed that closeness in R_f value of the reference sample and that of the *Parkia* dye point to the fact that some similarities exist between compounds in these samples. For example the R_f values of *Parkia* dye ranges between 0.28 – 0.86 while the reference sample has R_f value between 0.30 – 0.86. The closeness in R_f values of the various spots in the reference sample and the *Parkia* dye is also an interesting feature of the result obtained. The chromotogram also indicate that even the reference sample is not made up of chemically pure compound.

It can be observed that the chromatogram of the raw material (*Parkia* extract) shows only a single spot whereas the chromatogram of the product shows several spots. This invariably means that some kinds of reactions must have occurred during the coupling process giving rise to the product (*Parkia* dye). A plausible diazonium coupling reaction with condensed tannins can be represented by the equation presented below:

It is probable that a cheap coupling component in dye manufacture is feasible, since the fruit husk of *Parkia* used in the process is readily available.

Polyphenol (Condensed Tannin)

Diazonium Salt

Azo Dye

Conclusion

Results of the study, especially the infrared spectroscopy and chromatographic analysis show that some similarities exist between the coupled *Parkia* extract (*Parkia* dye) and the conventional dye, which was used as the reference sample. This points to the fact that naturally occurring polyphenols from plants such as *Parkia clappertoniana* can also be used as coupling component in the synthesis of azo dyes. Though, encouraging results were obtained in this study, it is however not conclusive. Dyeing trials can be carried out using the unconventionally prepared *Parkia* dye to ascertain the depth of colour and its substantiveness.

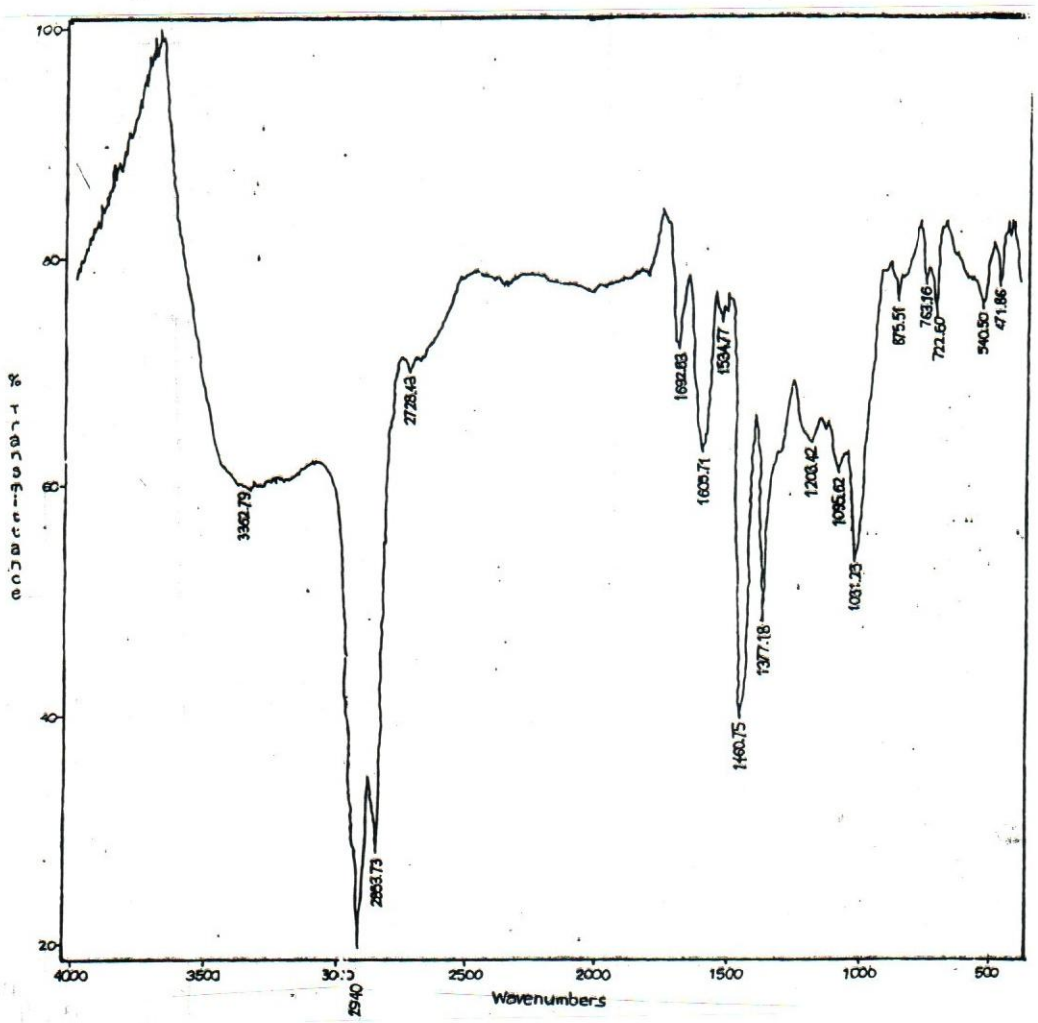

Figure 1: Infrared Spectrum of *Parkia* Extract

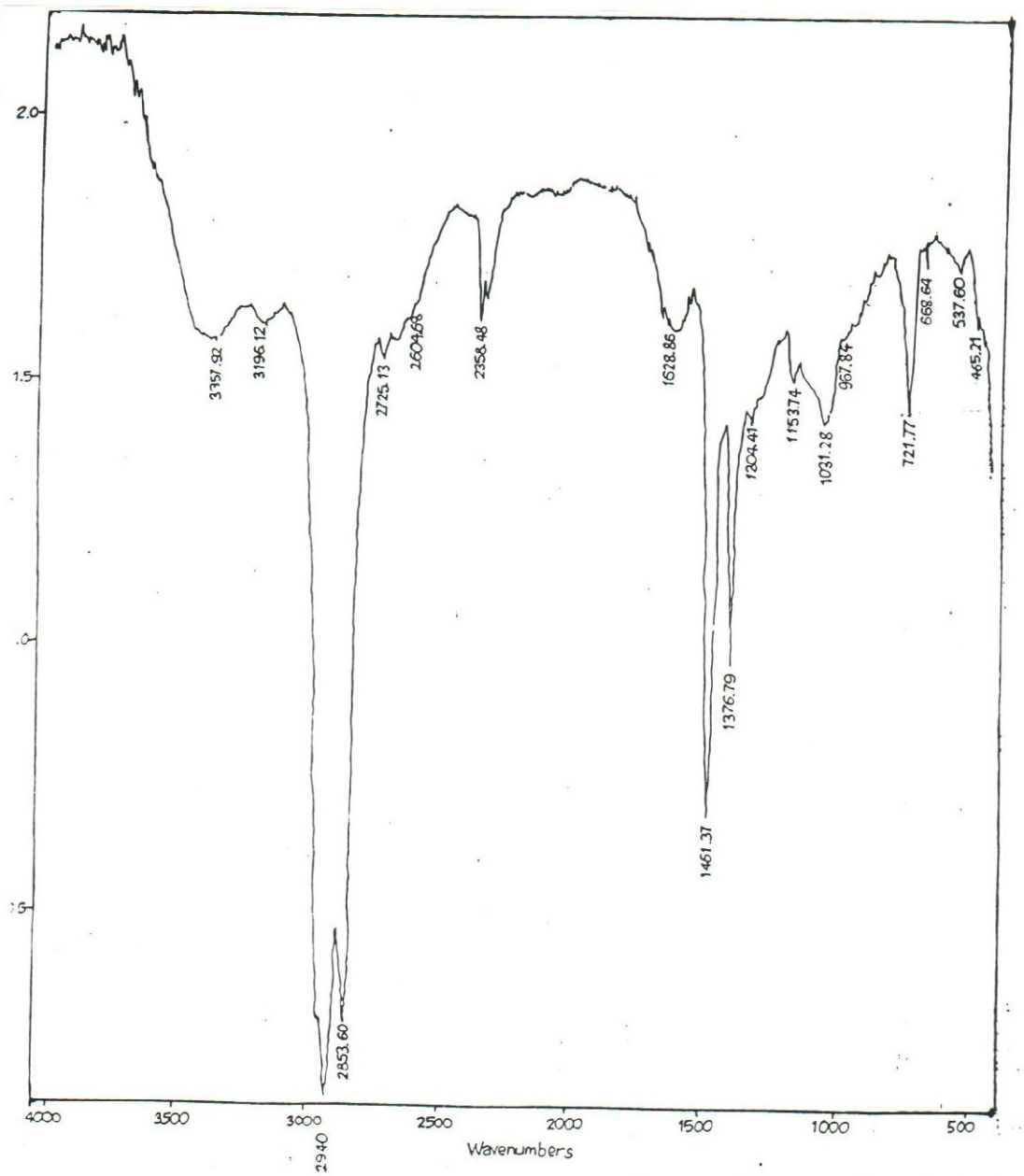

Figure 2: Infrared Spectrum of Coupled *Parkia* Extract (*Parkia* dye)

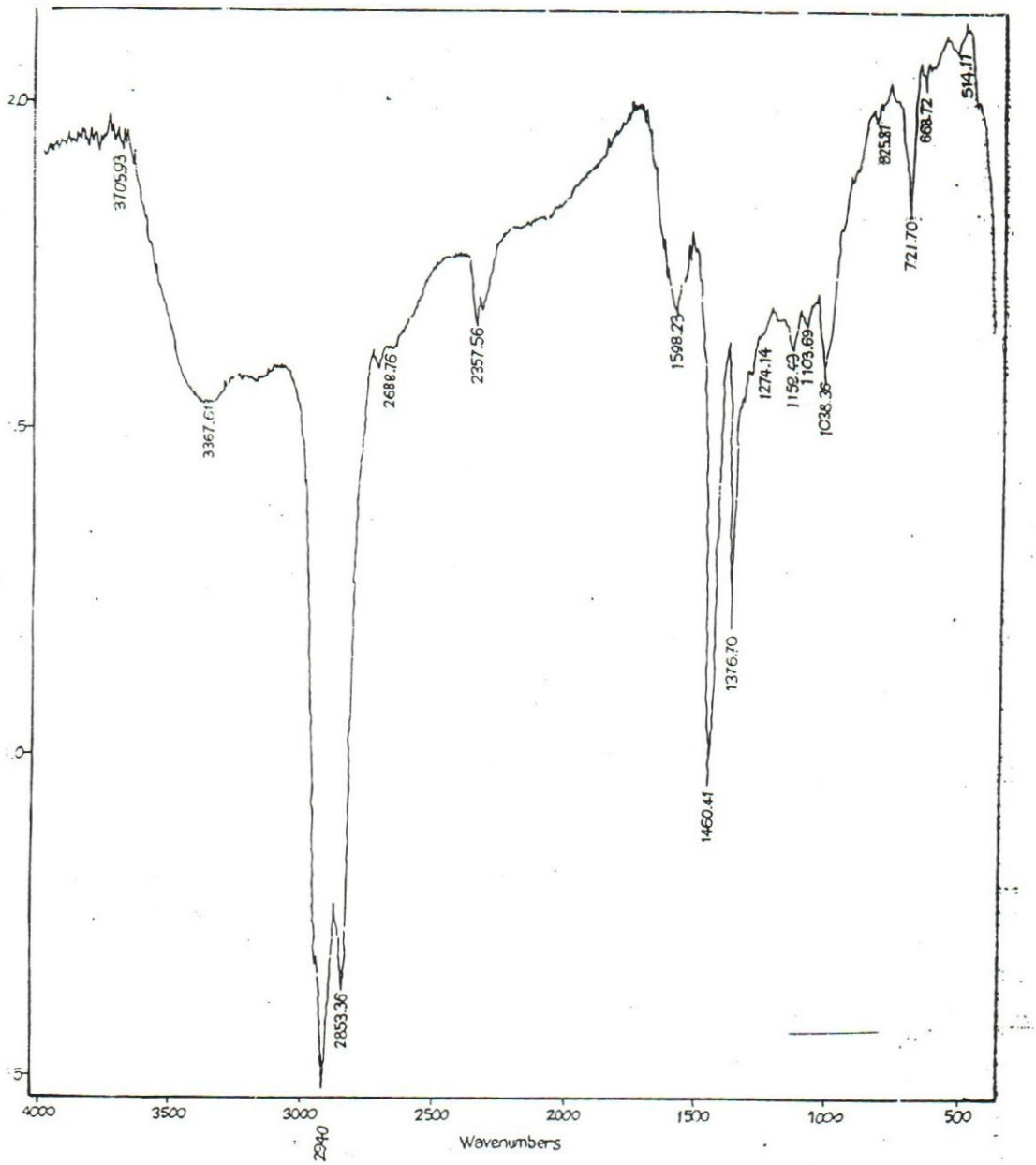

Figure 3: **Infrared Spectrum of Reference Sample**

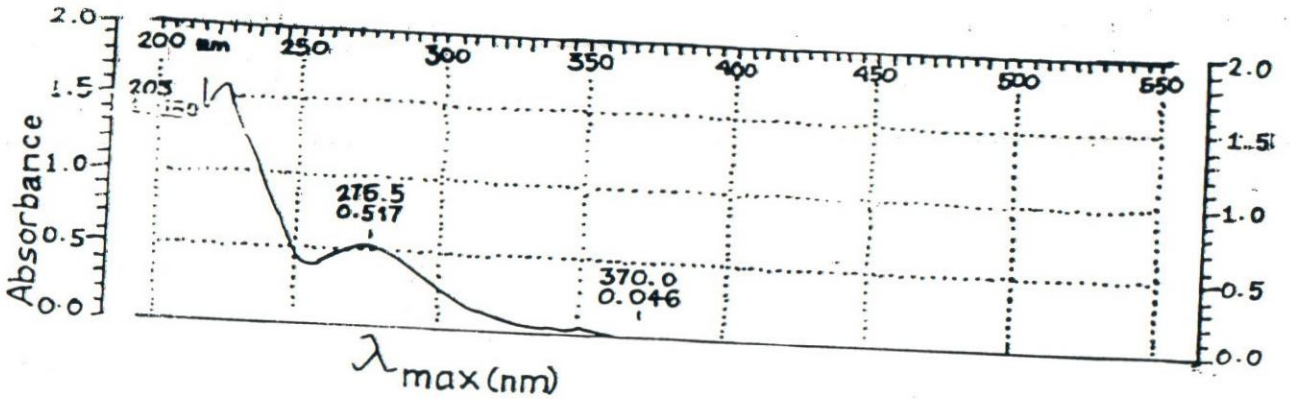

Figure 4a: Ultraviolet Spectrum *of Parkia* Extract

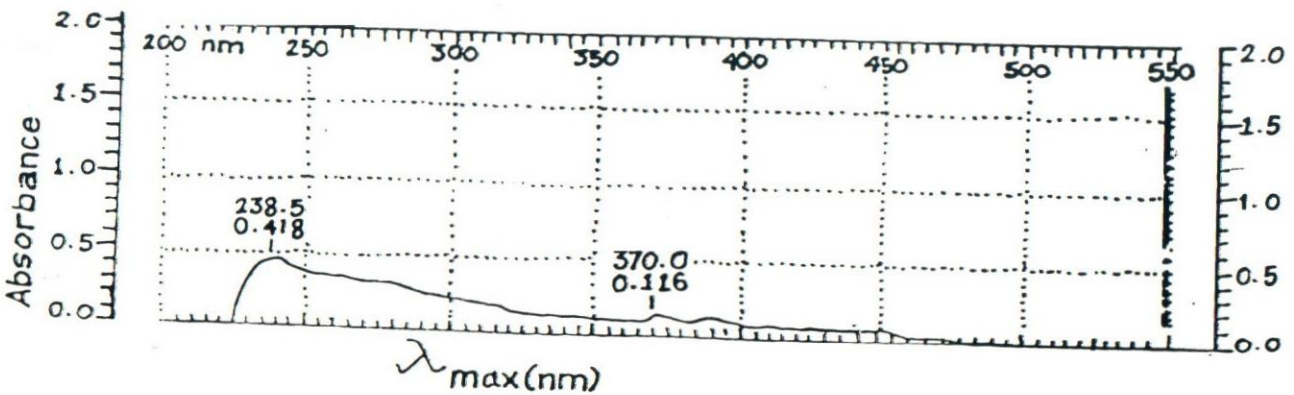

Figure 4b: Ultraviolet Spectrum *of Couple Parkia* Extract (*Parkia* dye)

REFERENCES

1. Stawari, K.S., Mehrota, S.N., Vishnoi N.K. (1977). A textbook of Organic Chemistry. pp. 1040 – 1042.

2. Kent, J. A. (1962). Reigel's Industrial Chemistry. Reinhold publishing cooperation, park avenue, New York pp 813.

3. Brown, G. I. (1984). New Introduction to Organic Chemistry, Longman Publishers, pp. 345 – 348.

4. Finar, I. L. (1996). Organic Chemistry, Vol. 1. Fundamental Principles, 64th edition, Longman Singapore publishers; Singapore, pp. 705

5. Hunt, A. (1998). The Complete A – Z Chemistry handbook, Greengate. Publishing Services, London.pp. 620 – 624.

6. Eital, K., Rau E., Westphal, J. (1994). Review of progress colouration of Leather. Society of Dyers and colourist, Perkin House, Bradfort. pp. 119 – 121.

7. Opara, E. N., Ukoha, P. O., Echewe, H. I. (2001). Study of Modified Extract from *Lawsonia inermis* for dyeing chrome – tanned leathers in aqueous media. Journal of Chemical Society of Nigeria. 26 (I): 39

8. Dalziel, J. M. (1937). Useful Plants of West Africa. Crown Agents for Overseas Government and Adminis-tration London. pp. 218.

9. Adewoye, R.O., Ajayi, O. (1987). Phenolic Constituent of *Parkia clappertoniana* Fruit Husk. Journal of the Society of Leather Technologist and Chemists. 72: 27.

10. Williams, D. H., Fleming, I. (1980). Spectroscopic Methods in Organic Chemistry, 3rd edition. pp. 35 – 63.

11. Morrison, R.T., Boyd, R.N. (1996). Organic Chemistry 6th edition. Prentice-Hall International (U.K.) Ltd., London. pp. 872.

12. Randerath, K. (1968). Thin Layer Chromatography. Academic Press. New York and London.pp107-112.