Characterisation of Colourant Extracted from Almond Leaves

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ABSTRACT

This research reports on the extraction of colourant from the almond leaves, Terminalia catappa using ethanol, methanol and water as solvents .This study indicates that these dye compounds can be selectively extracted with solvents such as Distilled Water, Ethanol and Methanol. Methanol was found to be the most suitable solvent for the extraction of dye compound from Terminalia cattapa leaves. It reveals the presence of chromophores of dye compounds in the leaf. This study also reveals the presence of the hybridized ketone groups, Quinone as the central group in the dye compound extracted. The presence of the aromatic groups, derivatives of benzene and naphthalene were also demonstrated. Other chromophoric groups identified by this study are N-H, CH_3, O-H, C=O, =C–NH and O-H polymeric stretch. The critical conjugated groups present in the extract include derivatives of Ketone, Quinone, an Aromatic secondary amine N-H, C-C of the benzene ring. Others include C-O Alkyl substituted ether, O-H polymeric stretch, C-N and C-O-C cyclic ether ring. The presence of the derivatives of Quinone as indicated by the Infra-Red spectra and the maximum absorbance at the Violet, Blue and Green wavelength ranges suggest a possible presence of a mixture of dye(s) with a central Quinone ring; hence, a possible presence of an anthraquinone, naphthaquinone and/or indigoid dye.

INTRODUCTION

Although dyeing of textile fabrics with dyes obtained from various natural resources has been extensively investigated, little information is available on the identification and characterization of the natural dyes[1]. Natural dyes, being plant metabolites, are present only in small amounts in dye-bearing materials along with large quantities of other nondye materials. The dye content may vary according to the age, part of the plant, and agroclimatic conditions[2], and it is important to know the dye content in order to get reproducible shades. While procuring the dye materials, pricing should match the dye content and when powdered dye materials or extracts are used, these should be authentic[3,4]. Thus determination of dye content as well as characterization of dye material is important in

the case of natural dyes[5,6]. Absorption spectroscopy is very successfully used for measuring the dye content of synthetic dyes but has limited applicability for natural dyes as these dyes are usually not a single chemical entity but a mixture of closely related compounds and in many cases there are no clearly defined absorption maxima[7]. A literature survey shows that the earliest attempts to characterize the natural dyes were made in the context of identifying the dyes present on historical textiles kept in museums or those found in archaeological excavations[8]. Different techniques including high performance liquid chromatography (HPLC), thin-layer chromatography (TLC), high-performance thin-layer chromatography (HPTLC), UV visible, and mass spectroscopy have been employed for this purpose[9]. Characterization of natural dyes is very important for the sustainability of true natural dyed textiles. TLC and HPTLC techniques can be easily employed for quick identification of natural dyes by comparing with chromatographic fingerprints of authentic natural dye samples. Many organizations have worked in this direction and in authors' lab HPTLC fingerprints of root and stem samples of Rubia cordifolia and Rubia sikkimensis were also developed[10]. A dye can be defined as a highly coloured substance used to impact colour to an infinite variety of materials like textiles, paper, wood, leather, plastics etc. As far as the chemistry of dyes is concerned, a dye molecule has some principled chemical groups, viz chromophores and Auxochromes. The chromophores, usually an aromatic ring, possesses colouring property, it has unsaturated bonds such as – C=C, =C=O, -C-S, =C-NH, -CH=N-, -N=N- and –N=O, whose number decides the intensity of the colour [11,12.] The auxochrome the dye molecule to combine the substrate, thus imparting colour to the latter.

As dyes have complex chemical structures, colour index has been developed for identifying the dyes. Based on their chemical and trade name in colour index, dyes are classified according to method of application. Within the application class, the dyes are arranged according to the hue. Dyes whose chemical structure is known are also given a constitution number that denotes their chemical constitution and also a name in the colour index which denotes the types of dye[13]. For example, the CI natural indigo hue is 75780 with the name CI number natural blue 1 in 1 is the identifying number[14]. The identification of natural dyes found in plants and how to extracts dyes from them have been a major interest[14]. The manufacture of synthetic dyes has been found to be energy intensive with adverse impact on environment, in addition to its pollution, serious health hazards like allergy, have been associated with the synthetic dyes.

This study is aimed at determination of the chemical constituents of colourant from almond leaves, *Terminalia catappa* through characterization of the colourant extract which can lead to formulation of its structural formula.

MATERIALS AND METHODS

Collection of Materials

The principle of collection of the raw material at the right time for obtaining a good result was observed. Leaves of *Terminalia catappa* were collected by August when the predominant

colour was green. Due to the fact that there was abundant supply of *T. catappa* leaves, samples were collected early in the morning and immediately processed, without the need of storage before analysis.

Identification of the Material

The material, *Terminalia catappa* leave, that was used for the study was identified by using the standard botanical identifying features.

Extraction of dye (colourant)

Extraction of dye (colourant) from the raw material is done by soaking the flakes of the material in a solvent such as water, chloroform etc and then reflux for about three hours.

Extraction: 50g of *Terminalia catappa* leaves flakes was weighed using an electronic weighing balance. The weighed samples were put into the empty beaker of 1000ml capacity. 500ml of distilled water was added into the beaker containing the flakes using a measuring cylinder. It was stirred continuously for one hour, after which the colourant extract solution (mixture) was poured through fine sieve mesh (to remove unwanted shaft), which was done at room temperature. The filtrate was kept for further analysis. Analysis (characterization) was carried out within 24 hrs after completion of the extraction process. The same procedure was used for the other solvents.

Characterization of Dye

Ultraviolent visible absorption (UV/VIS) and infrared spectroscopes are proven valuable tools for the characterization and identification of compounds, or functional group chemical bonds present in an unknown mixture of plant extracts[15]. They are used as qualitative tool to identify and characterize molecular species or some of their properties like molecular structure and characteristic absorption spectra that at least constitute their characteristic finger prints[16]. The infra-red spectral assignment of unsaturated bond of unknown samples determines the chromophore in the active compound[17]. The uv/vis is recorded by irradiating with uv/vis light that is continuously varied in wave length. When the wave length corresponds to the homo and lumo orbital of a conjugated system, some of the radiation is absorbed by the samples.

The extract from distilled water (dye) was spotted on the glass bowl using a spatula. The glass bowl was covered and fixed into infrared spectrometer machine; a beam of infrared was scanned through the extract for 5minutes. The infra-red spectral was obtained. The same procedure was used for the extracts from the other solvents.

Table1: Summary of Extraction Protocol

S/N	Solvent Used	Weight of material	Volume of solvent	Volume of extract	Temperature	Time
1	Distilled water	50g	500ml	486ml	27°C	24hrs
2	Ethanol	50g	500ml	447ml	27°C	24hrs
3	Methanol	50g	500ml	450ml	27°C	24hrs

RESULTS AND DISCUSSIONS

TABLE 2: UV/VIS Spectrophotometry Result for Distilled Water Extract

S/N	Wavelength (nm)	Absorbance	%Transmittance	Peak #	Group Present
1	250	0.663	21.73	-	
2	350	1.386	4.11	1	Naphthalene
1	405	3.775	0.02	2	Ketones
2	450	3.179	0.07	3	Ketones
3	490	2.105	0.78	4	Ketones
4	630	0.916	12.13	-	,

TABLE 3: UV/VIS Spectrophotometry Result – Methanol Extract

S/N	Wavelength (nm)	Absorbance	%Transmittance	Peak #	Group Present
1	250	1.703	1.98	1	Benzene
2	350	1.826	1.49	2	Naphthalene
3	405	3.900	0.01	3	Ketones
4	450	3.799	0.02	4	Ketones
5	490	2.313	0.49	5	Ketones
6	630	0.971	10.70	-	

TABLE 4: UV/VIS Spectrophotometry Result – Ethanol Extract

S/N	Wavelength (nm)	Absorbance	%Transmittance	Peak #	Group Present
1	250	0.073	84.53	-	
2	350	0.152	70.47	-	
3	405	3.905	0.01	1	Ketones
4	450	3.819	0.02	2	Ketones
5	490	3.843	0.01	3	Ketones
6	630	2.383	0.41	-	

TABLE 5: Infra –Red (IR) Spectral Results – Ethanol Extract

Peak #	Position	Height	Functional Group
1	3440.51	17.17	O-H
2	2857.00	15.00	C- H (Methylene)
3	1621.50	16.30	C=C stretch
4	1200.00	15.00	C-C Stretch

TABLE 6: Infra –Red (IR) Spectral Results – Methanol Extract

Peak #	Position	Height	Functional Group
1	3750.00	18.00	N- H (Aromatic secondary Amine)
2	3421.50	0.50	O-H (Normal polymeric Stretch)
3	2200.00	12.30	C-N
4	1621.50	16.30	Quinone
5	1444.04	14.70	C-C of Benzene
6	1265.00	13.89	C-O stretch
7	1187.00	12.58	C-O-C (Cyclic ethers, large rings)
8	1056.00	8.90	C-O (Alkyl –substituted ether)

Table7 Infra-Red (IR) Spectral-of extracts Using Distilled Water

Peak #	Position	Height	Functional Group
1	2700.00	0.60	Aldehyde
2	1637.50	3.481	C=O
3	1265.00	8.70	C-O stretch
4	1056.00	8.90	C-O (Alkyl –substituted ether)

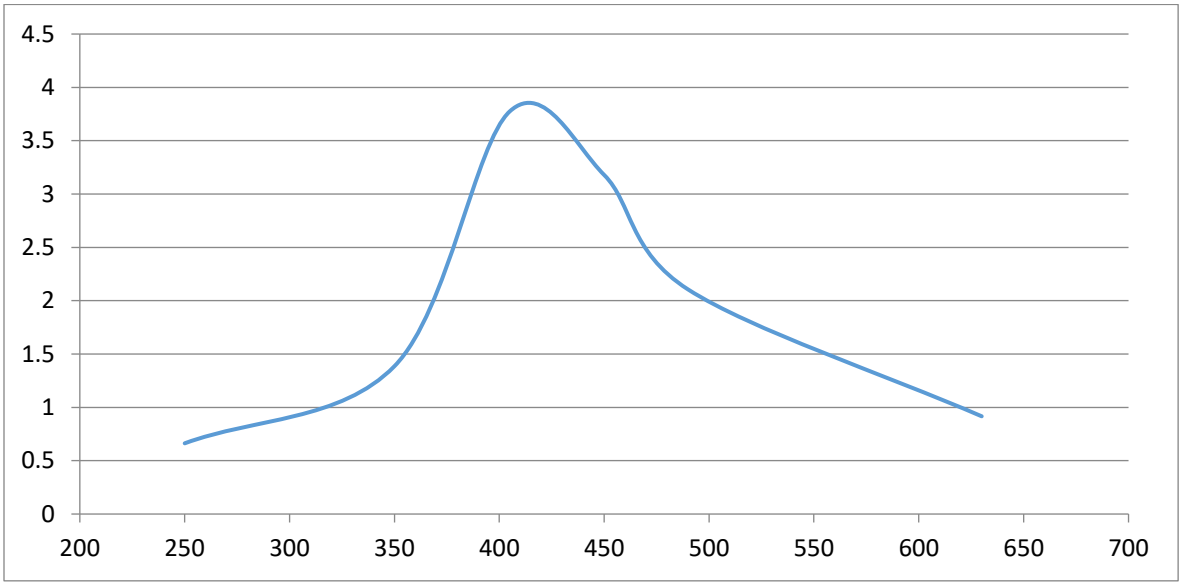

Fig 1: Absorption spectra per wavelength range Distilled Water Extract

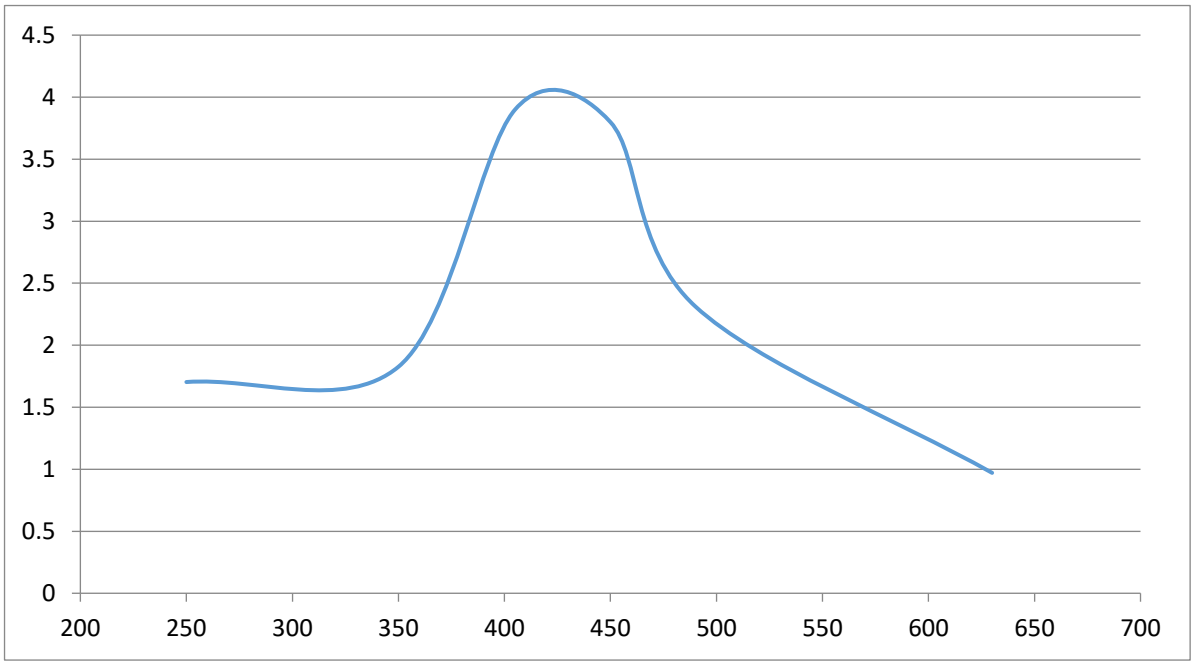

FIG.2: Absorption spectra per wavelength range – Methanol Extract.

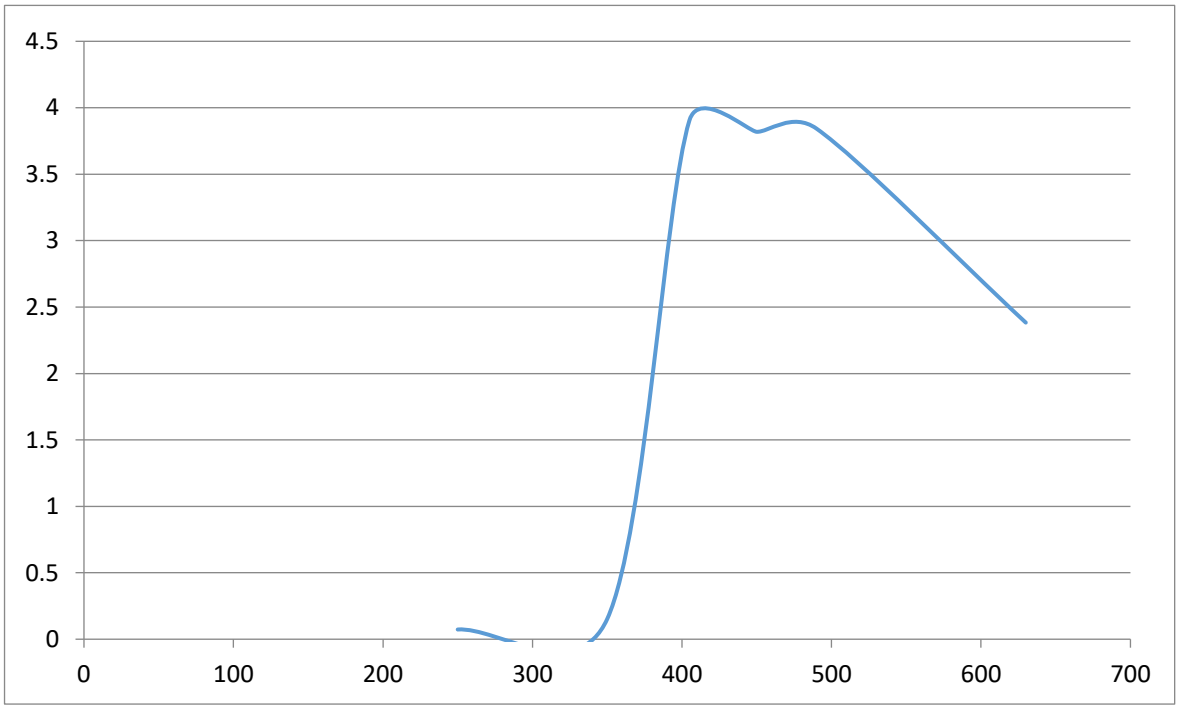

FIG 3 : Absorption Spectra Per Wave Length Range Ethanol Extract.

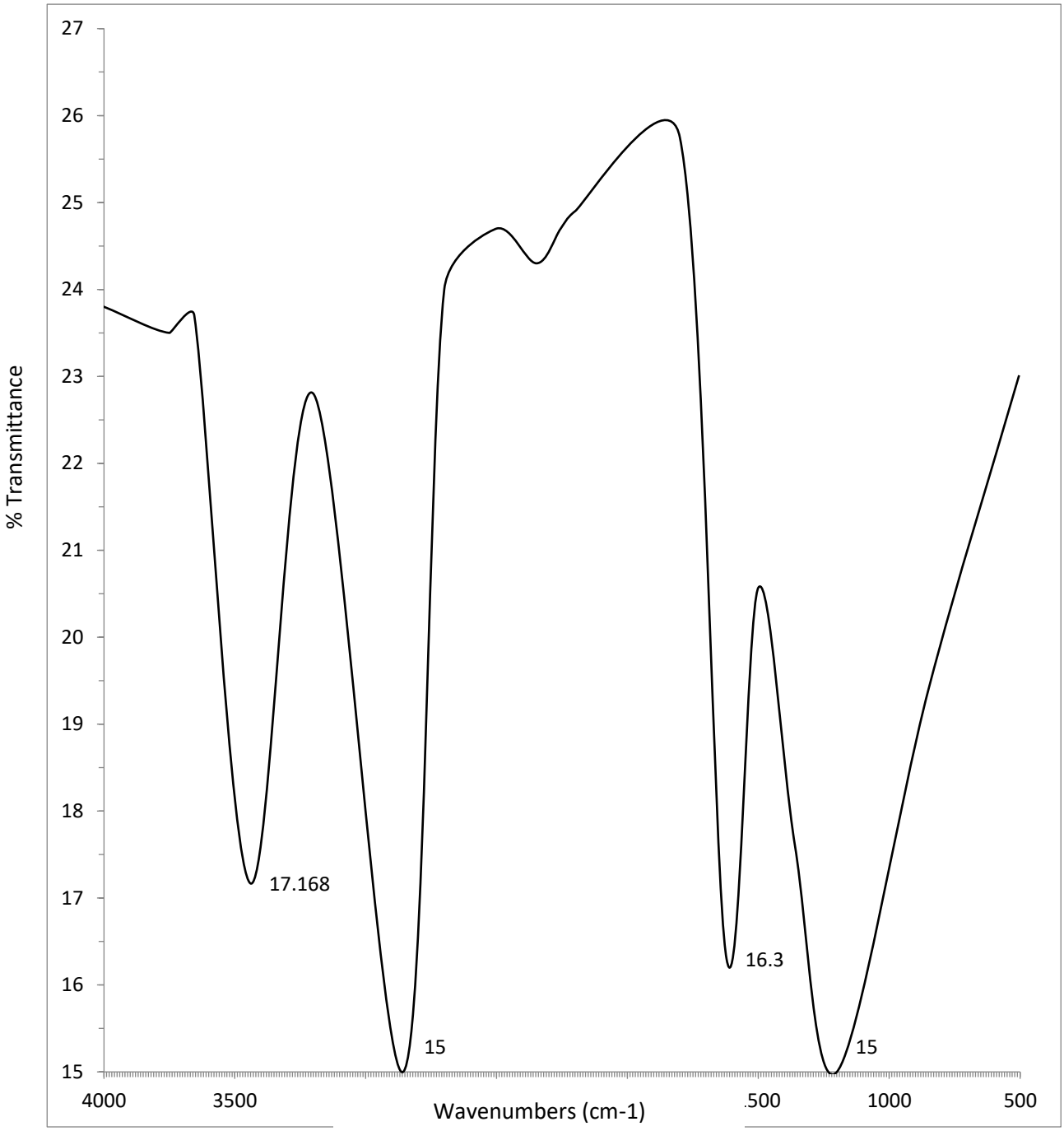

FIG 4: Absorption Spectra Per Wavelength Range-Ethanol Extract.

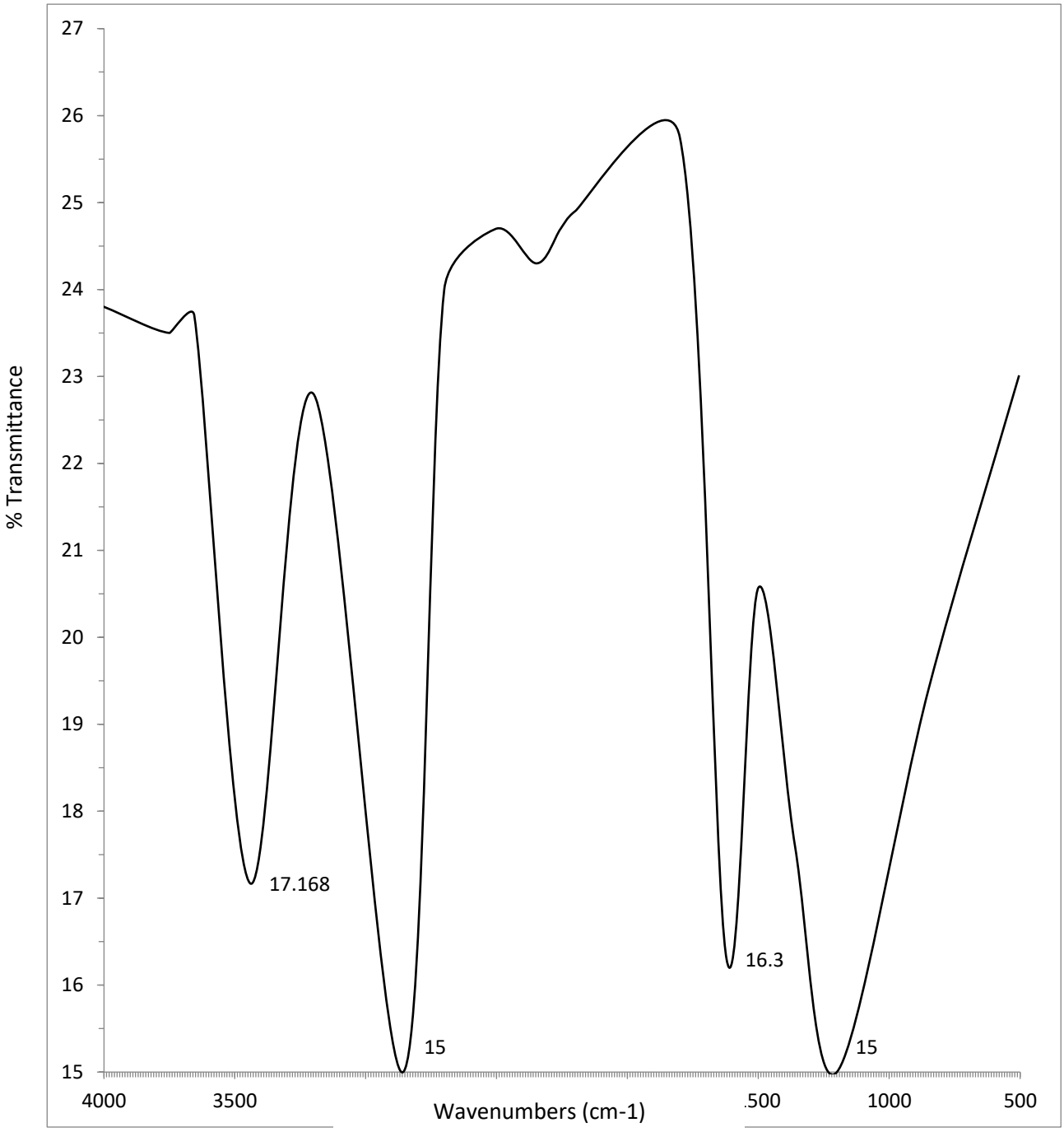

FIG.5: Peak finding results for: Ethanol Extract

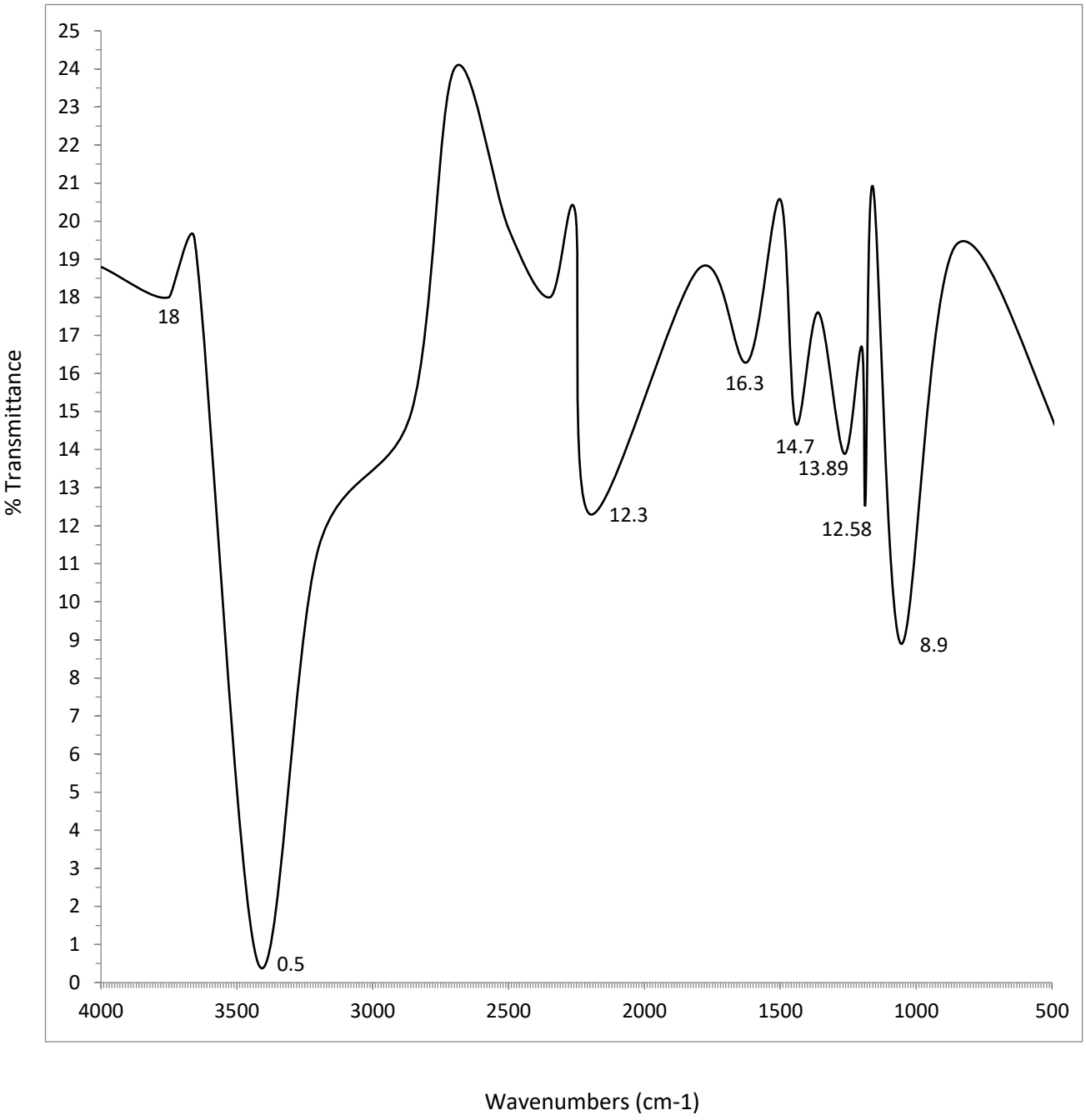

FIG. 6: Peak finding results for: Methanol Extract

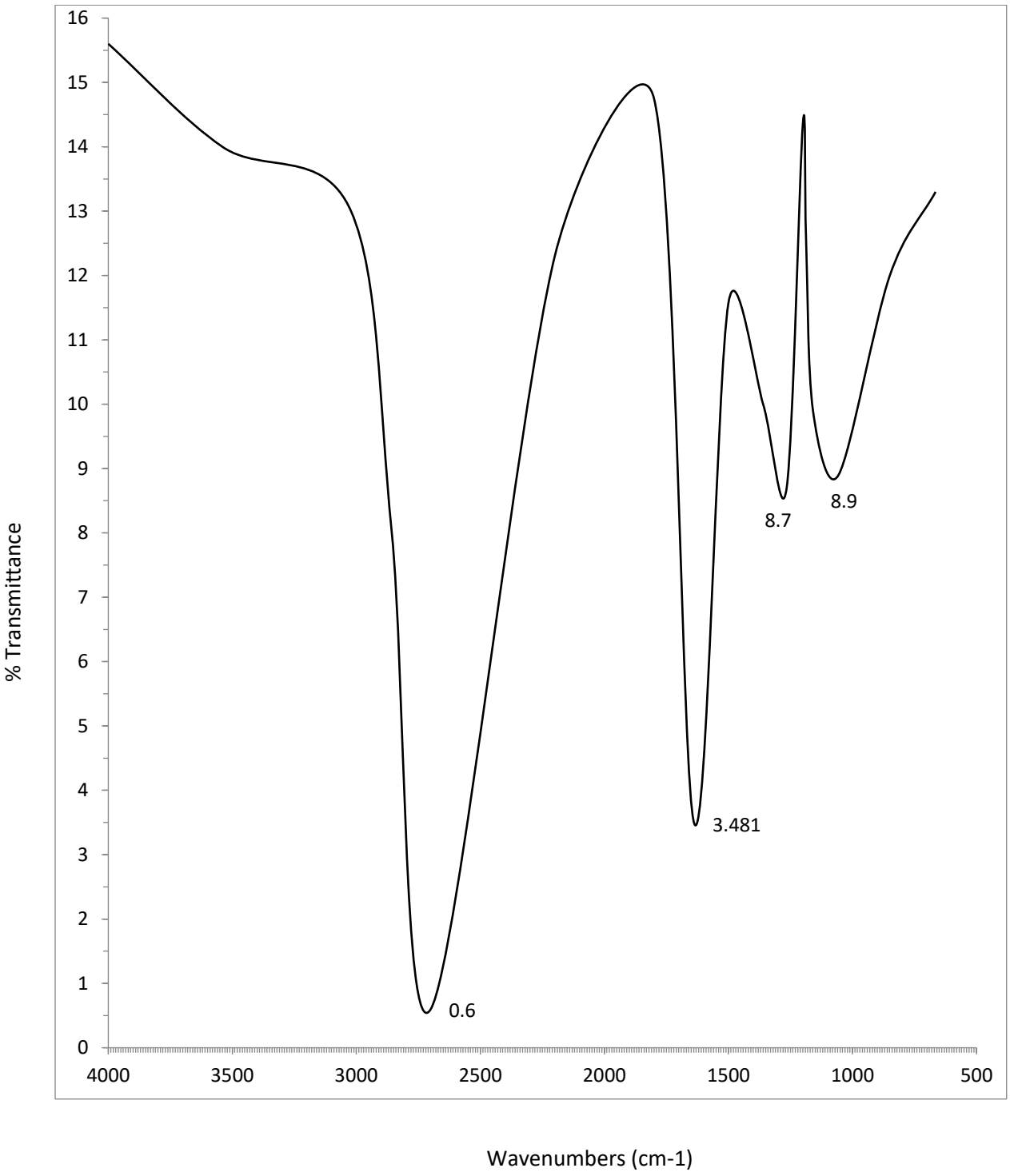

Fig. **. 7: Peak finding results for: Distilled Water Extract**

Distilled Water, Ethanol and Methanol were the 3 solvents used for the extraction in equal volume of 500mls. The extraction result as shown in Table 1.1 reveals that Distilled Water has the highest yield of extract (486ml). This is followed by Methanol and Ethanol extracts with a yield of 450ml and 447ml respectively. The difference in volume of yield extract might be based on the volatility of Ethanol and Methanol in comparison with Distilled Water at the temperature the extraction was carried out.

The absorption spectral of the different extracts; Methanol, Ethanol and Distilled Water; across the Ultra Violet and Visible wavelengths measured are as shown in Table 2, 3 and 4. The observed absorbance reveal the highest values at the 405nm, 450nm and 490nm in the visible wavelength range across all the different extracts studied. This indicates that the greater volume of compound present in the different extracts from Methanol, Ethanol and Distilled Water is Ketone. However some iota of Naphthalene was also observed from the Distilled Water and Methanol extracts while Benzene was observed only in the Methanol extract.

A graphical representation of the Methanol, Ethanol and Distilled Water extracts (Figure I, II & III) indicates the highest absorbance at 405nm wavelength. The similarity in the maximum wavelength of absorbance for the different extracts at the Ultra Violet and Visible wavelength ranges indicates that the components have similar chromophore and hence, contain similar chemical compounds.

The result of the UV/VIS spectrophotometry and the observed maximum wavelength (405nm, 450nm & 490nm) of the extracts implies the necessary condition for the formation of colour mixtures of Violet, Blue and Green absorbance.

The Infra-Red spectral assignments of unsaturated bonds of the extract are presented in Tables 5, 6 & 7 for Ethanol, Methanol and Distilled Water extract respectively. The results reveal the type of chromophores in the active dye compound. The critical conjugated groups present in the extract include Quinone, an Aromatic secondary amine N-H, C-C of the benzene ring. Others include C-O Alkyl substituted ether, O-H polymeric stretch, C-N and C-O-C cyclic ether rings.

Class of Dye Extract

The presence of the Quinone as indicated by the Infra-Red spectral and the maximum absorbance at the Violet, Blue and Green wavelength ranges suggest a possible presence of a mixture of dye(s) with a central Quinone ring; hence, a possible presence of an anthraquinone, naphthaquinone and/or indigoid dye.

As revealed by the Infra-Red and UV/VIS spectra, the dye extract could have the following structures.

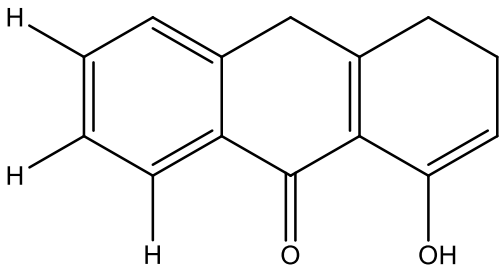

Figure 7: Possible Structure I for Dye extract

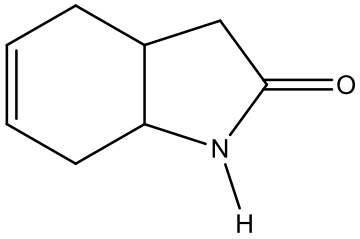

Figure 8: Possible Structure II for Dye extract

CONCLUSIONS

The research carried out on the characterization of extracts of *Terminalia cattapa* leaf reveals the presence of chromophores of dye compounds in the leaf. This study also indicates that these dye compounds can be selectively extracted with solvents such as Distilled Water, Ethanol and Methanol. Methanol was found to be the most suitable solvent for the extraction of dye compound from *Terminalia cattapa* leaves. This study also reveals the presence of the hybridized ketone groups, Quinone as the central group in the dye compound extracted. The presence of the aromatic groups, such as the derivative of benzene and naphthalene were also demonstrated. Other chromophoric groups identified by this study are N-H, CH_3, O-H, C=O, =C–NH and O-H polymeric stretch.

Lastly, this study suggests 3 likely types of dye compounds in the *Terminalia cattapa* leave extract, these are: anthraquinone, naphthaquinone and indigoid dyes.

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