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Extraction and Application of Natural Colourant from the Bark of *Berlinia Grandiflora* on Cotton and Polyamide 6 Fabrics

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Abstract

The aim of this study is to extract and utilise the bark of *Berlinia grandiflora* as a natural dye source for the colouration of cotton and polyamide 6 fabrics. The solvents used for this study were water, methanol, acetone, and methanol/potassium hydroxide. The best of all the solvents used was water. In the extraction process, the various solvents were extracted with Soxhlet extractor. The optimum colourant extraction was observed at 40 °C for 2 h. The extracted compound was isolated and characterized by UV spectrophotometry; proton and carbon-13 nuclear magnetic resonance, mass spectrometry, and Fourier transform infrared spectroscopy. Mordanting and subsequent dyeing of cotton and polyamide 6 fabrics with the extracted colourant were performed to investigate the dye's efficiency. Two metal salts, namely copper sulphate and stannous chloride, were used as mordants. Furthermore, the washing, rubbing, and light fastness properties of dyed samples were tested. The results of the fastness tests showed that the natural dye gave light fastness value (3= fair) without the use of mordants, whereas the values were 5 on cotton and 4 on nylon 6 with the use of mordants. The results of fastness of rubbing and washing were excellent for both cotton and nylon. The outcome of the study presents a potentially useful natural colourant for the colouration of natural and synthetic fibers.

Keywords: *Berlinia grandiflora*, natural dye, extraction, mordant dyeing, exhaustion, fastness.

1.0 Introduction

In the earliest years of the colour industry, environmental issues have always been a cause for concern. This has led various governments to issue laws and edicts on detection and quantification of even tiniest contaminants that may be present in both industrial products and wastewaters [1-4]. Out of these, there is a particular concern over the impact of the chemical industry and its associated products on the environment [5]. The application of dyes and pigments is of rising interest in the recent time. It is evident that the price of synthetic dyes and pigments is increasing by the day due to high cost of intermediates and increasing environmental costs. Some dye manufacturers have even been forced to stop producing due to shortage of raw materials [6-8].

Some colourants from plants, such as combretum, latifolium, frazinifolia, and pomegranate rind can be regarded as safe alternatives to the use of synthetic dyes and pigments due to their low toxicity and biodegradability. Thus, research is on-going towards identifying sustainable and more environmentally friendly materials in terms of natural dyes for use in textile dyeing and printing industries [9-11]. Current applications of natural colourants to textile fibers are in the area of ink-jet printing and screen printing [1, 12, 13]. In this case, printing of textiles with natural dyes is related to dyeing. However, during dyeing, the bulk of the fabric is uniformly covered. During printing, one or

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more colourants are applied to a particular part of the fabric with patterns to create attraction from the consumer.

Berlinia grandiflora (Family: *Caesalpiniaceae*) is a green forest leguminous plant. It is widely available in Nigeria, Guinea, Mali, Central Africa, and Democratic Republic of Congo [14]. Rural folks in eastern Nigeria use the sap extract in treating wounds and sores. The leaf and bark extracts of this tree have also been used in treating some ailments like liver problems, nausea, vomiting, and as analgesic to relief pain [15-16]. The wood from this tree is used for construction purposes such as house building, ship building, furniture, plywood, and other similar applications. However, no study was made on the application of the colourant from *Berlinia grandiflora* on textile fibbers. Therefore, the main aim of the present study is to utilise the bark extract of this tree as a source of natural colourant for the coloration of cotton and polyamide 6 fabrics. This is done in order to explore more industrial uses of the plant. The effects of mordanting, sunlight, and fastness of light, rubbing, and washing were assessed to judge the practicability of the application. Moreover, an attempt was also made to evaluate the exhaustion of the extracted colourant on the cotton and polyamide 6 fabrics for a better standardization and comparison of results.

2.0 Materials and Methods

Methanol, acetone, potassium hydroxide, ethanol, silica gel, chloroform, stannous chloride, copper sulphate, acetic acid, and sodium sulphate were all obtained from Sigma-Aldrich Chemicals Company, UK. Industrially bleached woven cotton fabric (100%) and polyamide 6 were purchased from a local market in Nigeria. A dye master dyeing machine from Zaria, Nigeria as well as a Jenway 6405 UV-visible spectrophotometer and a crockmeter (RossariLabtech, Q-Lab, Corp., USA) were used for testing, while ^{1}H NMR, ^{13}C NMR spectra were recorded using a Mercury 200 BB series NMR spectrometer (USA) with tetramethylsilane (TMS) as the internal standard reference. The used solvent was deuterated dimethylsulphoxide (DMSO-d_6). All the chemical transitions in delta (δ) were in parts per million. The FT-IR values were measured in cm^{-1} while mass was measured in m/z.

2.1 Study Zone

The reason for choosing *B. grandiflora* among hundreds of plants is because of its ease of accessibility which could be important for its application in the textile industry. The bark of *B. grandiflora* was collected from Delta State (Obiaruku), Nigeria. The herbarium of the plant was authenticated by a taxonomist at the University of Calabar, Nigeria (Voucher number = 2016/Cal/HRB/1243).

2.2 Extraction of Colourant

To extract the colourant from the plant, 10g of powder (ground) was extracted with 300mL of distilled water at various temperatures (20, 40, 60 and 80 °C). They were also placed into a Soxhlet device for extraction at 100 °C for 1 hour each. Extraction was also carried out at 70 °C at various times of 1, 2, 3, and 5 hours, respectively. Other solvents, such as methanol, acetone, and methanol/potassium hydroxide were used for the extraction. Plots of absorbance of dye against temperature or time were recorded. All the colourant extracts using water as solvent were then collected and subjected a distillation procedure under a vacuum until a 300mL solution was obtained. Flash column chromatographic analysis (ethanol-chloroform solvent system, 4:1) was used to separate and isolate one component of the natural colourant and was confirmed using thin-layer-chromatography to give one spot of R_f value of 0.8 after repeated separations. This obtained component was characterised using ^{1}H NMR, ^{13}C NMR, FT-IR, GC/MS, and Mass Spectrometry which were used to measure the main functional groups of the colourant.

2.3 Fabric Treatment

The polyamide 6 fabrics were scoured using 1.0 gL^{-1} of non-ionic detergent (DiadavinUN from Resin Saveh, Iran) for 20min at 60°C and liquor ratio of 40:1. The cotton fabrics were equally scoured in a solution containing 3% sodium hydroxide and 3% scouring agent (soap flakes, 5.0 g and sodium carbonate 1.5 gL^{-1}) at 100 °C for 60 mins [27].

2.4 Direct Dyeing

The pre-treated cotton and polyamide fabrics (1.0 g) were each dyed in separate dye baths without mordants. Dyeing was carried out with a liquor ratio of 1.50 using a 2% shade of weight of fabric at 85 °C for 1 h in a standard laboratory dye master dyeing machine. After 30 mins of dyeing, 3.0 g sodium sulphate was added to improve exhaustion. The samples were then removed, washed with distilled water, and dried at 50 °C [28].

2.4.1 Mordant Dyeing of Polyamide 6

The mordanting baths was prepared using two different mordants, which are stannous chloride (4%) and copper (II) sulphate (6%), by adjusting the pH to 5 using acetic acid. The initial temperature of the mordanting bath was set at 40 °C and it was brought to boiling over 20 mins and held at 100 °C for 1 h [28].

The dyeing process with the extracted compound was started at 40 °C, and the temperature was increased to 100 °C over 20 mins and held at this temperature for 1 h. All the samples were rinsed with cold water to remove dyes from the surface and dried at room temperature.

2.4.2 Mordant Dyeing of Cotton

The scoured cotton fabrics were rinsed in water, cut into 10 x 10 cm pieces, and weighed. Dye extract (100 ml) was placed in the dye master dyeing machine and the mordanted cotton fabrics were dipped into the dye solution. Dyeing was carried out at 60 °C for 1 h, keeping a 1:50 material-to-liquor ratio. After dyeing, the samples were rinsed and dried at room temperature and used for further experiments. The extent of exhaustion obtained for 2% (of weight of fibre) dyeing on cotton and polyamide 6 fabrics was determined using spectroscopic analysis of the dye bath before and after dyeing.

2.4.3 Determination of dye exhaustion rate

To determine the dye bath exhaustion rate, 50 µL dye bath aliquots were removed, diluted to 6.0 ml, and absorbance measurements were carried out at the maximum wavelength of absorbance ($\lambda_{\max}$ = 420nm) using a Jenway 6405 UV-visible before and after dyeing. A linear response between absorbance (0.01) and concentration (0.08) was observed for the diluted dye solution. The measurement was carried out three times and then the average was obtained. Hence, the dye exhaustion rate in terms of percentage exhaustion (%E) was calculated using the following equation [17].

$$\%E = \left(1 - \frac{A_1}{A_0}\right) \times 100 \qquad ------------ (1)$$

where A_0 and A_1 are the absorption values of dye solution before and after dyeing, respectively.

2.5 Assessment of fastness properties

Dyed samples were tested in accordance with the ISO standard test methods [18].

2.5.1 Washing Fastness

The washing fastness properties of the dyed samples was measured according to ISO, 105-C10: 2006[19]. The test samples were washed in a soap solution, held at 60 °C for 30 min, and the extent of staining on the adjacent undyed fabrics was evaluated using a standard grey scale (1-5), where 1 is poor and 5 is excellent.

2.5.2 Light Fastness

In the case of the light fastness measurements, the dyed samples were exposed to daylight for 72 h in accordance with the ISO-B02: 2014 test method [18]. The changes in photo-fading were assessed according to a standard blue scale (1-8), where 1-2 is poor and 8 is excellent.

2.5.3 Rubbing Fastness

The dry and wet rubbing fastness of the dyed samples were assessed in accordance with the ISO 105-X12: 2016 test method (RoassaiLabtech, Q, Lab Corp, USA), [19] and the changes in colour were evaluated using a standard grey scale (1-5), were 1 is poor and 5 is excellent.

3.0 Results and Discussion

3.1 Dye Extraction

According to Otutu *et al.* [20], dye extraction of colourants at 70°C for 4 h is applicable to produce an optimum amount of natural dye in water [21]. Figures 1 - 10 show the effects of extraction temperature and time on the extracts. It can be seen that, when the extraction time was 3 h, the absorbance increased as the extraction temperature was raised to 40 °C. However, when the extraction temperature was higher, the absorbance decreased. The method involved the use of water that includes other additives, such as KOH, or other solvents, such as acetone and methanol. The extraction efficiency did not significantly increase when water alone was used. Hence, the natural dyes existing in the plant bark powder were easily dissolved into the extracting water, leading to an increase in the absorbance of the extract.

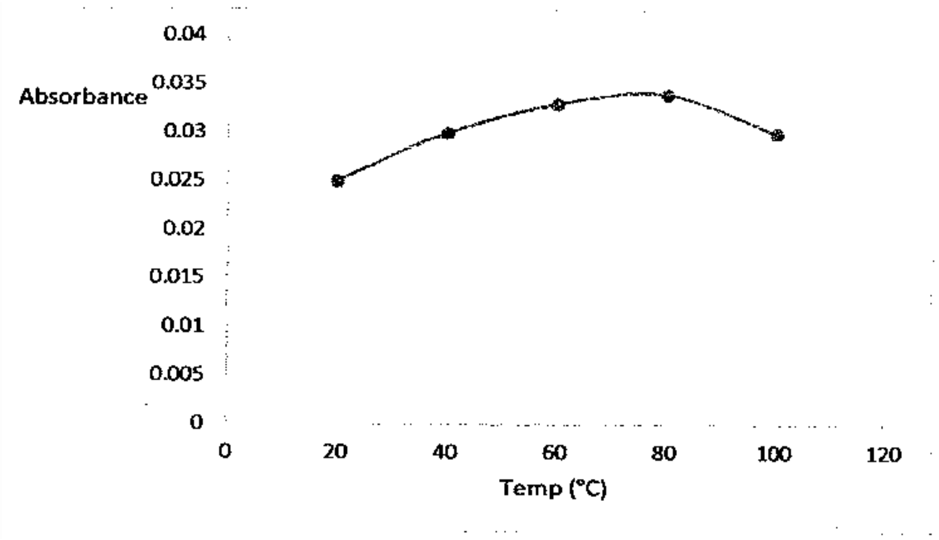


Figure 1- Effects of extraction temperature on the absorbance of natural colourant from Berlinia grandiflora using acetone as solvent

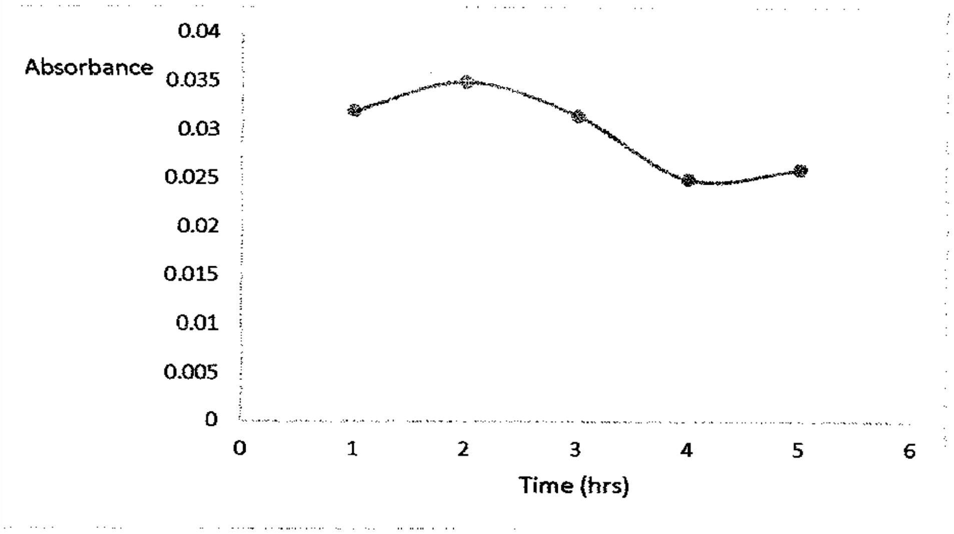


Figure 2- Effects of extraction time (in hours) on the absorbance of natural colourant from *Belinia grandiflorta* using acetone as solvent at 70 °C.

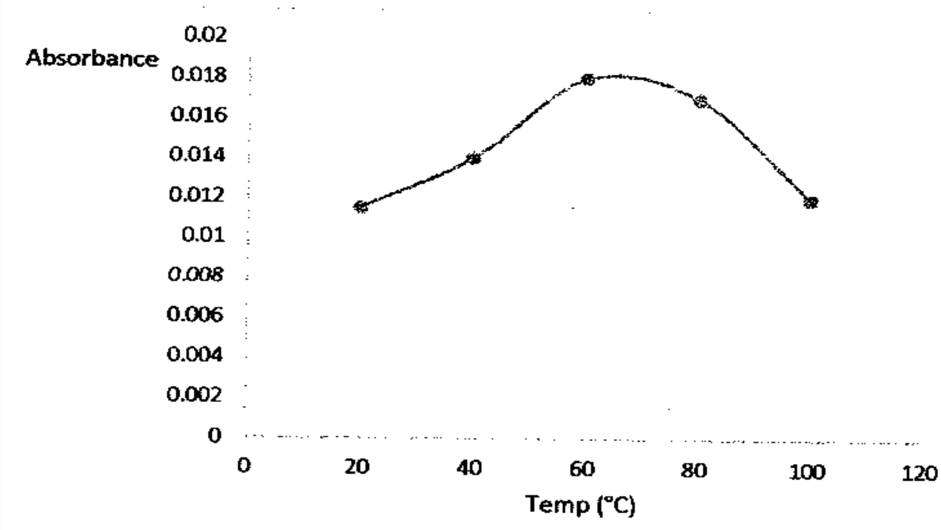


Figure 3-Effects of extraction temperature on the absorbance of natural colourant from *Berlinia grandiflora* using methanol as solvent.

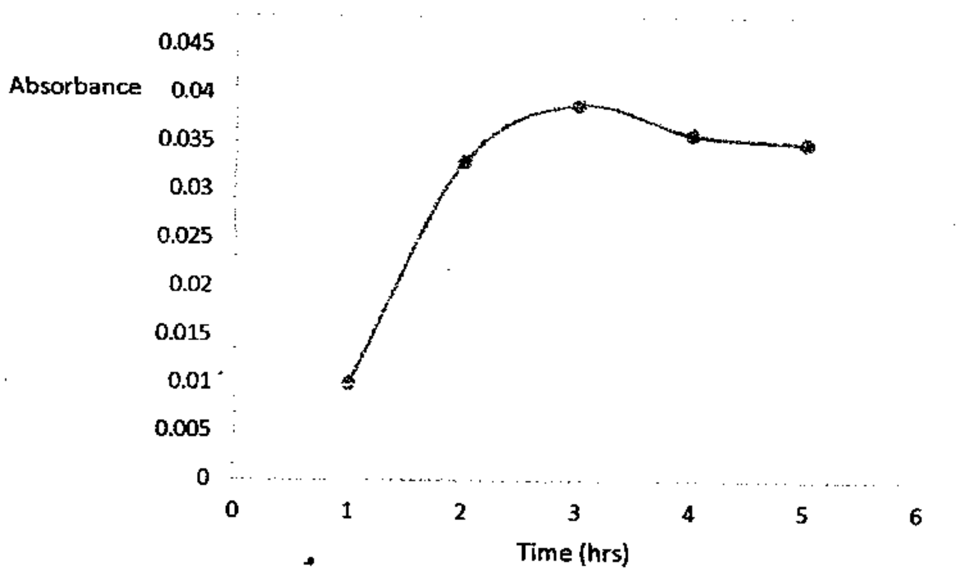


Fig. 4- Effects of extraction time (in hours) on the absorbance of natural colourant from *Belinia grandiflorta* using methanol as solvent at 70 °C.

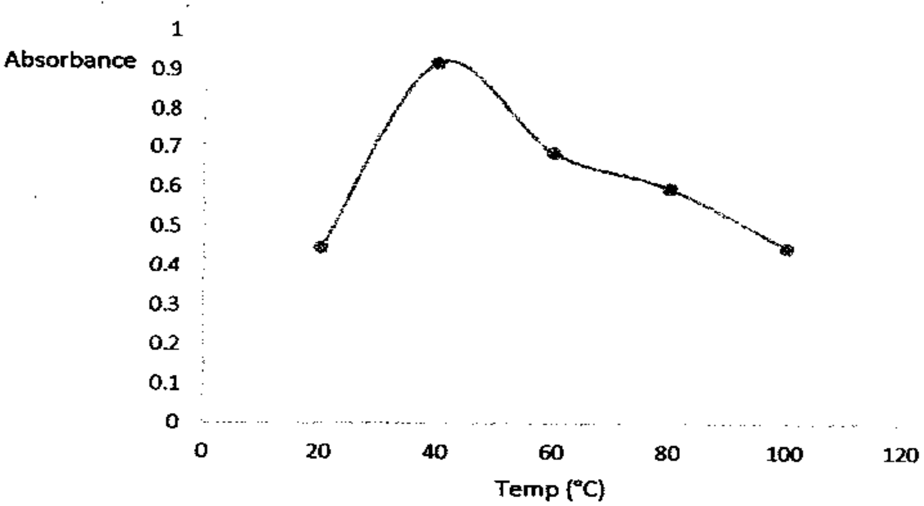


Figure 5-Effects of extraction temperature on the absorbance of natural colourant from *Berlinia grandiflora* using water as solvent.

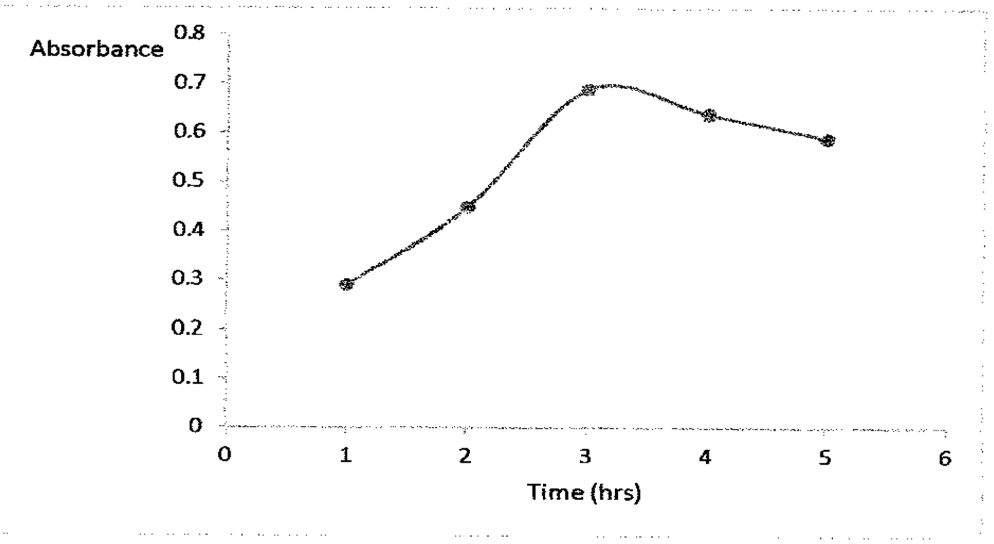


Figure 6-Effects of extraction time (in hours) on the absorbance of natural colourant from *Belinia grandiflorta* using water as solvent at 70 °C.

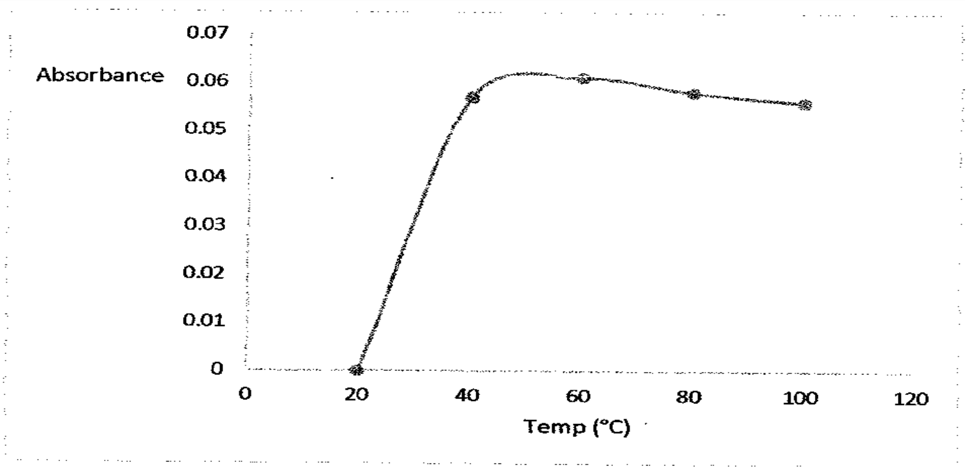


Figure 7- Effects of extraction temperature on the absorbance of natural colourant from *Berlinia grandiflora* using $KOH_{(aq)}$ and acetone as solvents.

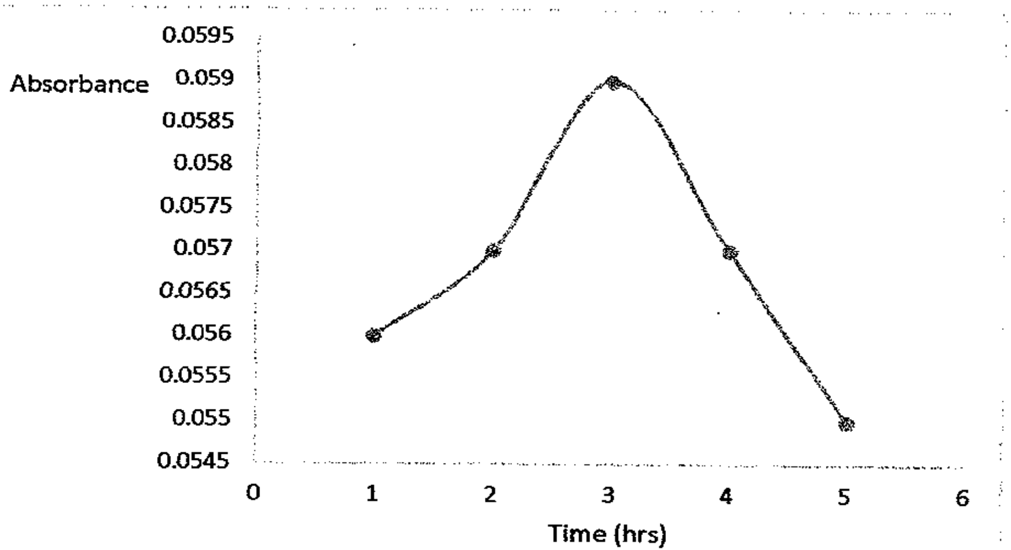


Figure 8-Effects of extraction time (in hours) on the absorbance of natural colourant from *Belinia grandiflorta* using $KOH_{(aq)}$ and acetone as solvents at 70 °C.

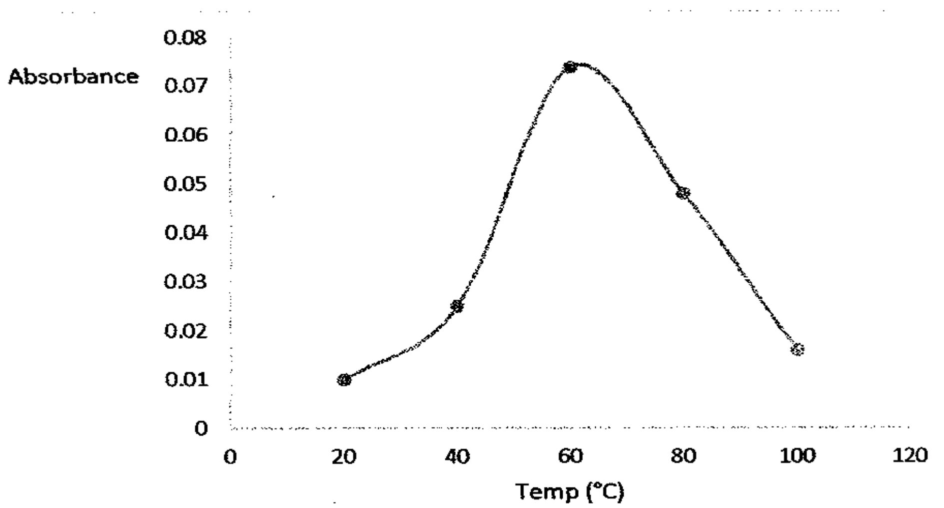


Figure 9- Effects of extraction temperature on the absorbance of natural colourant from *Berlinia grandiflora* using $KOH_{(aq)}$ and methanol as solvents.

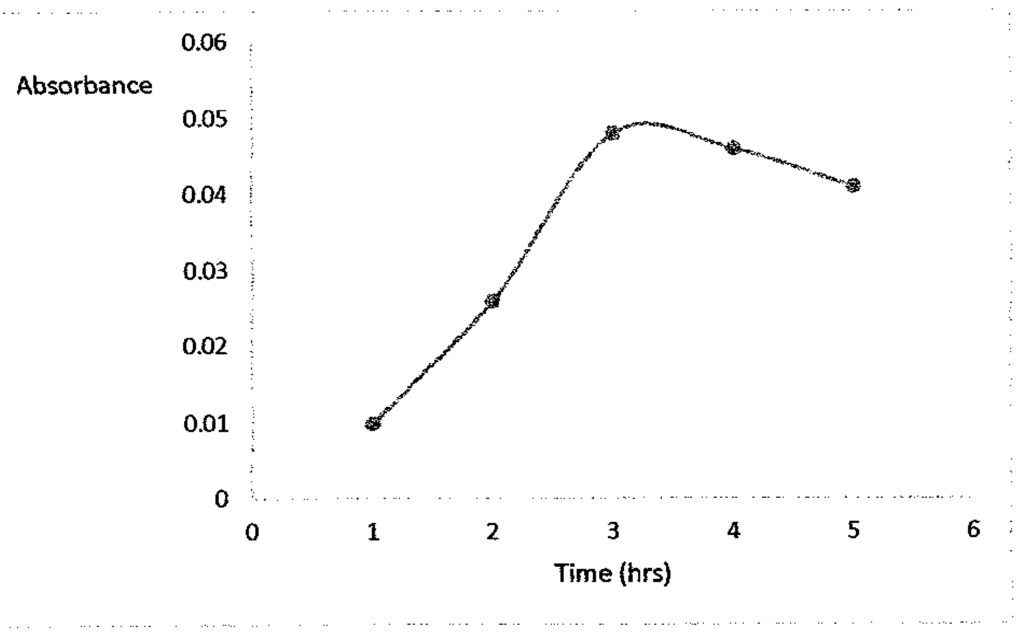


Figure 10-Effect of extraction time (in hours) on the absorbance of natural colourant from *Belinia grandiflorta* using $KOH_{(aq)}$ and methanol as solvents at 70 °C.

3.4 Characteristic of the dye extract

Table 2-Spectral data of an isolated component of the colourant

FTIR(cm^{-1})	3444($O\text{-}H_{str}$), 2955($C\text{-}H_{str}$), 2346-2125($C\text{-}H_{deform}$), 1647($C=0_{str}$), 1401 ($C\text{-}H_{bending}$), 1057($C\text{-}O_{str}$), 546-392 (C-O-R), 392 (R-O-R)
^{1}HNMR δ(ppm)	1.28-1.38(CH_3), 3.73-3.77(OCH_3), 5.69-5.72(OH)
^{13}C NMR δ(ppm)	18.4(CH_3), 29.1, 29.3, 29.5, 29.7, 29.8(ALL CH_2), 54.2($(OCH_3)_2$), 57.3(CH), 208(C=O)
Mass spectrometry (m/z)	95(8.44), 103(0.53), 110(1.12), 112(15.11), 122(2.73), 125(0.74), 126(2.62), 139(1.44), 163(5.65), 178(1.00), 178(2.76), 178(4.67), 178(5.39), 178(6.29), 205(3.86), 218(1.45), 218(2.70), 218(4.87), 224(2.26), 234(1.845), 236(1.80), 253(2.62), 256(5.87), 258(3.30), 260(4.11), 270(0.97), 284(3.42) M^+
UV-Visible	λ_{max} 371nm and 376nm Chromophores: -C=C-C=O and -C=C

The functional groups present in the natural colourant extracted from *B. grandiflora* were analysed using FTIR spectroscopy, as shown in Figure 11. In the spectrum of the colourant extract of *B. grandiflora*, a characteristic broad O-H stretching vibration was observed at 3444 cm^{-1}. The peaks at 2955, 2346, 2125 are due to stretching and deformation vibrations of C-H [24]. The stretching vibrations of C=O were found at 1647 cm^{-1}, indicating the presence of a ketone. The peak observed at 1401 cm^{-1} is attributed to C-H bending vibrations. The band at 1057 cm^{-1} demonstrates and confirms the presence of O-H in the colourant extract. The stretching vibrations at 546 cm^{-1} and 392 cm^{-1} might be due to the presence of esters. These results demonstrate the presence of phenolic and ester groups in the
colourant extract.

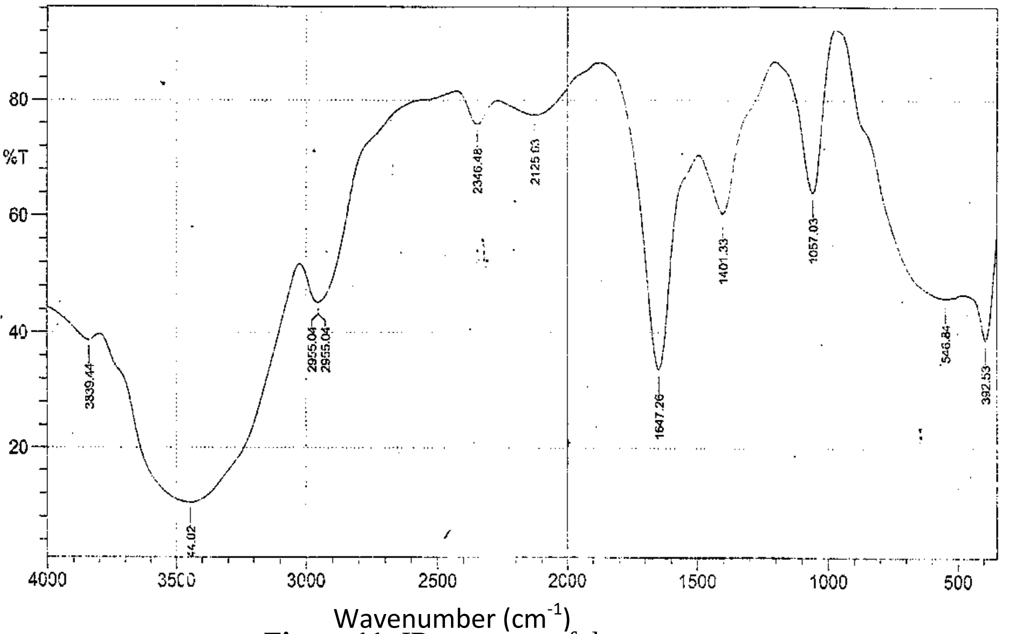
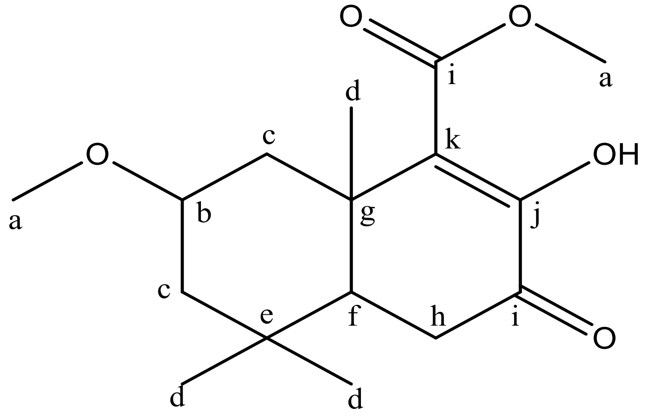


Figure 11- IR spectrum of dye extract

The absorption at δ 1.28 – 1.38 indicates CH_3 protons. The singlets at δ 3.73 – 3.77 suggest the presence of OCH_3 protons while the broad singlet at δ 5.69 – 5.72 is assigned to OH protons. The carbon-B spectrum of the colourant extract showed CH_2 (SP^3) carbons at δ 18.4. In addition, the peaks at δ 29.1, 29.3, 29.5, 29.7, 29.8 ppm indicate CH_2 (SP^2) carbons [24]. The absorptions observed at δ 54.3 and 57.3 ppm suggest the presence of CH carbons. The absorption observed at δ 208 is assigned to carbonyl (SP^2) carbons [25]. These results further confirmed the presence of a carboxylic acid group [26].

In the UV-visible spectrum of the natural extract, the bands at 371 nm and 376 nm are due to chromophores, including the C=C-C=O and C=O bonds. The mass of the isolated natural extract was found to have an m/z value of 270.



2-Hydroxy-5,5,8a-trimethyl-7-methoxy-3-oxo-3,4,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxylic acid, methyl ester.

Figure 12-Structure of the predicted dye extract from *Berlinia grandiflora,*

3.5 Fastness Properties

The washing fastness results are based on a set of 60°C standard laundering conditions given in Table 3. The washing fastness ratings for both fabrics were excellent, being rated at 4-5 or 5, indicating that the two mordants used for the study improved the washing fastness properties of the colourants on the fabrics.

Table 3-Colouring fastness properties of dyed and mordanted cotton and polyamide fabrics

Fabric Type	Samples	Rubbing Fastness		Washing Fastness		Light Fastness
		Dry	Wet	Colour Change	Staining	
Cotton	Unmordanted	3-4	3	2/3	3/4	3
Polyamide 6	Unmordanted	4	3	3	3/4	3
Cotton	Sn^{2+}	4	4	4	4/5	3/4
Polyamide 6	Sn^{2+}	5	4/5	4	5	3/4
Cotton	Cu^{2+}	5	4/5	5	5	5
Polyamide 6	Cu^{2+}	5	4/5	4/5	4/5	4

The dry and wet rubbing fastness showed ratings of 4-5 on cotton fabric and 5 on the polyamide 6 fabric, based on the standard grey scale, implying very good to excellent fastness properties with stannous chloride as mordant. However, the performance of the colourant during dry and wet rubbing with copper sulphate as the mordant was observed to be better compared with stannous chloride mordant.

The ability of a colourant on a dyed or printed fabric to resist the action of daylight is an important attribute of coloured textiles [29]. The light fastness results of the dyed cotton and polyamide 6 fabrics are shown in Table 3. The light fastness ratings of the colourants were observed to be 5 on cotton fabrics and 4 on polyamide 6 fabrics, based on the blue wool scale, when copper sulphate was used as the mordant.

However, the light fastness properties of the colourant when stannous chloride was used as the mordant were rated at 3-4 on both fabrics. The moderate light fastness properties of the colourant in the presence of copper sulphate mordant are attributed to the existence of Cu (II). This indicates that it has a co-ordination number of 6, which reflects practically the sites for interaction with the fibre. Light fastness is thus generally improved as the metal is Cu (II).

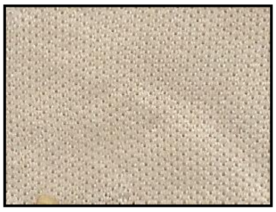
3.2 Mordanting

Since natural dyes commonly require a mordant treatment for adequate fixation on textile fibres, two mordants were selected and used for the dyeing process, which were stannous chloride and copper sulphate. Although the use of these mordants have been found to introduce some environmental consequences [22-23] as metal containing agents, their presence in the applied mordant bath was considerably reduced by the addition of acetic acid into the dyebath to enhance more metal fixation on the textiles. The percentage exhaustion data (Table 1) is in support of this. In this case, more metal is taken up by the fiber, making the spent mordant bath less harmful for disposal.

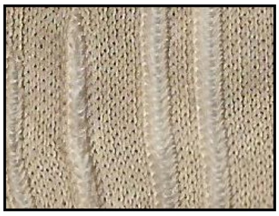
Non-mordanted cotton

Cotton pre-mordante with$CuSO_4$

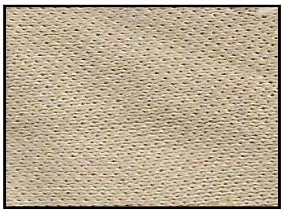
Cotton pre-mordante with S_nCl_2



Non-mordantedpolyamide 6



Polyamide 66 mordanted with $CuSO_4$



Polyamide 66 premondanted S_nCl_2

3.3 Dyeing and Percentage Dyebath Exhaustion

Table 1- Maximum exhaustion of colourant from *B. grandiflora* on cotton and polyamide 6 fabrics with and without mordanting

Dying method	Colourant exhaustion (%)
Cotton without mordant	58
Cotton mordanted with$CuSO_4$	80
Cotton mordanted with S_nCl_2	72
Polyamide 6 without mordant	51
Polyamide 6mordanted with $CuSO_4$	68
Polyamide 6mordanted with S_nCl_2	63

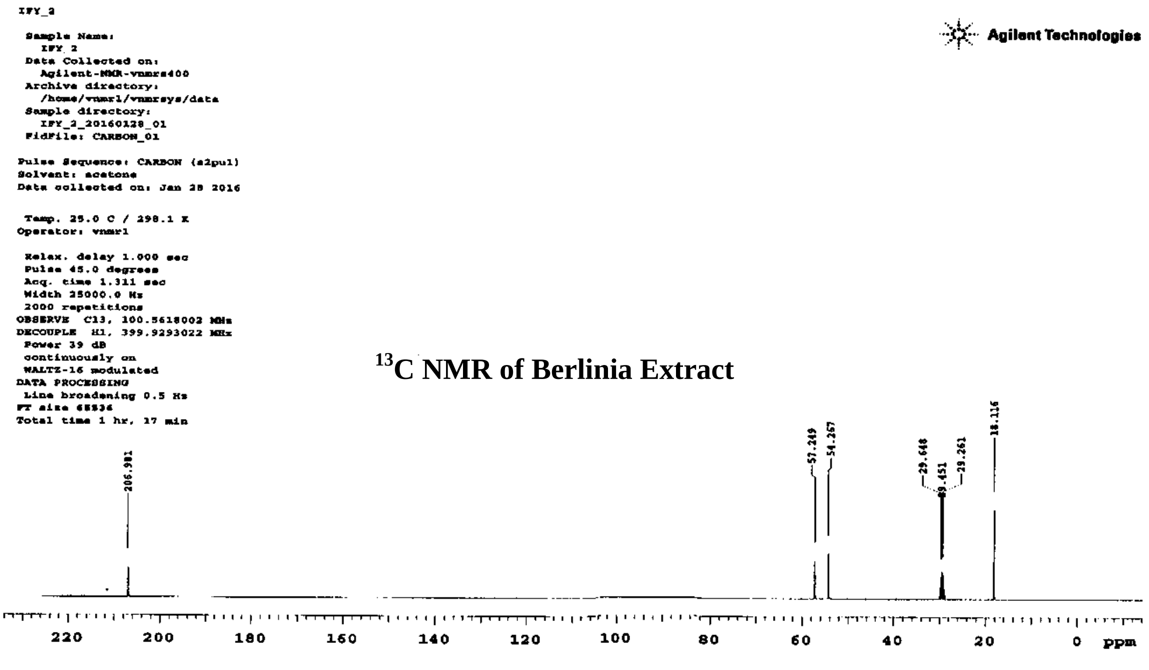
The natural colourant from *B. glandiflora* was applied to cotton and polyamide 6 fabrics at 2% (dye shade) using the dye master dyeing machine for 1 h. Brown shades were obtained. The dyeing properties on the two textile fabrics were evaluated in terms of their fastness properties (fastness to light, washing, and rubbing).

Colourant exhaustion into the fabrics was calculated and it showed very good results. The non-mordanted fabrics gave good exhaustion, with more than 50% of the dye exhausted to the fabric, while the mordanted fabrics showed better exhaustion compared with the non-mordanted fabrics, owing to the increased fixation of the dye to the fiber. The cotton fabric dyed with the colourant and treated with copper sulphate mordant gave a percentage exhaustion of 80% compared with stannous chloride 72%, while polyamide 6 fabric dyed in the presence of the same mordant gave a percentage exhaustion of 68% compared with stannous chloride which gave 63%. This indicates that copper sulphate is a better mordant compared with stannous chloride. The results also show that the colourants diffused and fixed more into the cotton fabric using copper sulphate compared with polyamide 6 fabric.

3.6 Conclusions

This study extracted a natural colourant from *Berlinia grandiflora.* The dye extracted was favoured by the use of water as extracting solvent. Spectroscopic studies of the dye showed that the compound is of octahydronapthalene derivatives of hydroxyl, methyl, methoxy, and oxo functional groups. The compound also exhibited good water, light, and rubbing fastness qualities. $CuSO_4$ and $SnCl_2$ are good mordants for dye extraction. The dye is brown in colour and suitable for the dyeing of cottons and polyamide fabrics.

Appendix 1



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 Sample directory:
   IFY_2_20160128_01
 FidFile: CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: acetone
Data collected on: Jan 28 2016

 Temp. 25.0 C / 298.1 K
Operator: vnmr1

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 2000 repetitions
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DECOUPLE  H1, 399.9293022 MHz
 Power 39 dB
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 WALTZ-16 modulated
DATA PROCESSING
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Total time 1 hr, 17 min
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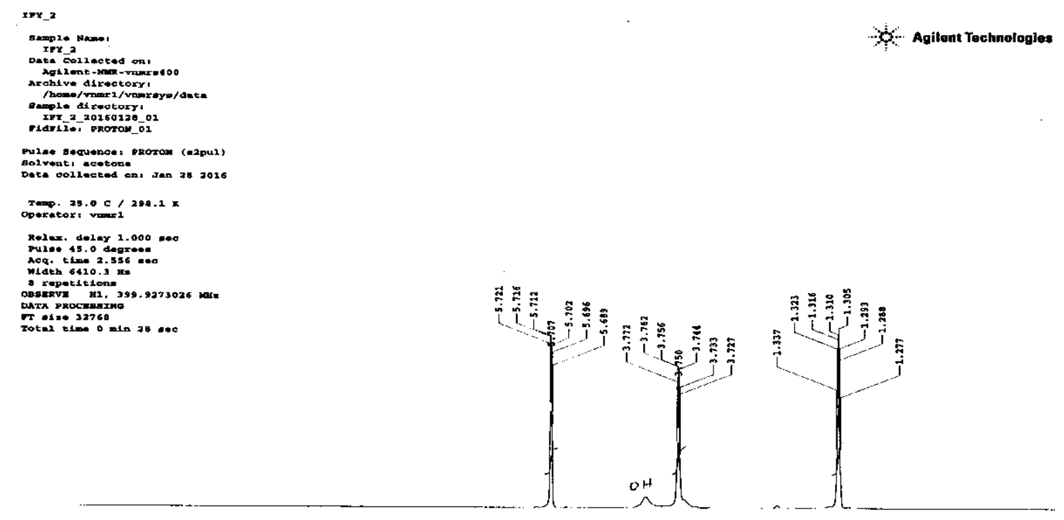
^{13}C NMR of Berlinia Extract



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 FidFile: PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: acetone
Data collected on: Jan 28 2016

 Temp. 25.0 C / 298.1 K
Operator: vnmr1

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 Acq. time 2.556 sec
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 8 repetitions
OBSERVE   H1, 399.9273026 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec
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^{1}H NMR of Berlinia Extract

Mass spectrometry information

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    SPL2                     : Yes
    MS                       : Yes
< Ready Check Detector(FTD) >
< Ready Check Baseline Drift >
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    SPL2 Carrier             : Yes
    SPL2 Purge               : Yes
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< Ready Check Detector APC Flow >
External Wait                :No
Equilibrium Time             :3.0 min

[GC Program]

[GCMS-QP2010 Plus]
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Interface Temp.         :250.00 °C
Solvent Cut Time        :2.50 min
Detector Gain Mode      :Relative
Detector Gain           :0.00 kV
Threshold               :1000

[MS Table]
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End Time                :28.00min
ACQ Mode                :Scan
Event Time              :0.50sec
Scan Speed              :1250
Start m/z               :40.00
End m/z                 :600.00

Sample Inlet Unit       :GC

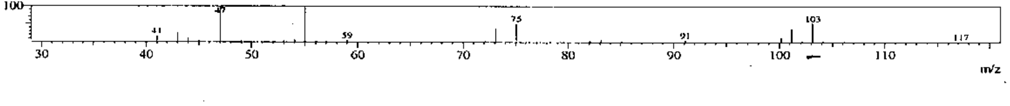
[MS Program]
Use MS Program          :OFF
```

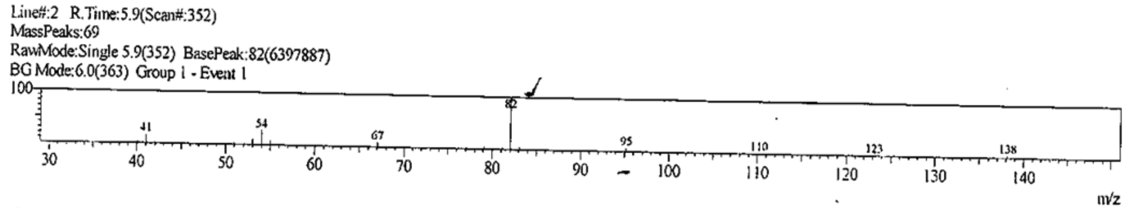
Peak Report TIC

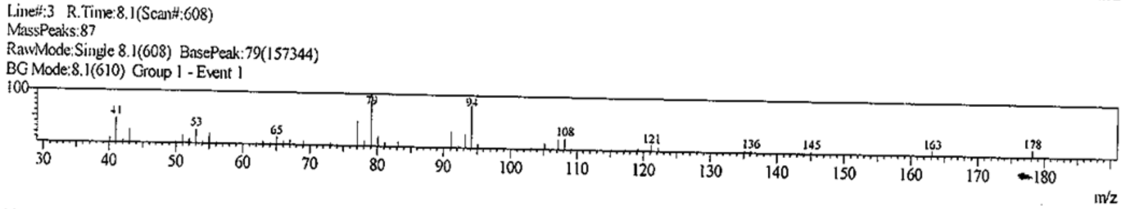
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.057	3.008	3.100	3848759	0.53	1039372	0.62	3.70		
2	5.930	5.842	6.108	61472741	8.44	16155833	9.63	3.80		
3	8.061	8.017	8.142	7251976	1.00	3232460	1.93	2.24		
4	8.751	8.700	8.875	10486202	1.44	3502534	2.09	2.99		
5	9.010	8.950	9.067	41171952	5.65	12478610	7.44	3.30	V	
6	9.223	9.142	9.392	45795142	6.29	10546901	6.29	4.34	V	
7	9.470	9.392	9.558	39271884	5.39	10650046	6.35	3.69	V	
8	10.193	10.125	10.258	34046536	4.67	10629382	6.33	3.20	V	
9	10.576	10.525	10.600	8139756	1.12	3210606	1.91	2.54	V	
10	11.132	11.008	11.183	20086251	2.76	5056605	3.01	3.97	V	
11	11.331	11.275	11.408	19668318	2.70	5844427	3.48	3.37	V	
12	11.557	11.517	11.667	17669219	2.43	5252854	3.13	3.36	V	
13	11.989	11.942	12.050	19886478	2.73	5283393	3.15	3.76	V	
14	12.377	12.342	12.442	13489445	1.85	4734231	2.82	2.85	V	
15	12.559	12.492	12.617	13087332	1.80	3346040	1.99	3.91	V	
16	13.158	13.117	13.275	10596527	1.45	2706931	1.61	3.91	V	
17	13.527	13.475	13.608	19077656	2.62	4991753	2.97	3.82	V	
18	13.850	13.767	14.008	35487587	4.87	7420708	4.42	4.78	V	
19	14.451	14.342	14.500	19107758	2.62	5692951	3.39	3.36	V	
20	14.910	14.725	15.025	24027017	3.30	4682235	2.79	5.13	V	
21	15.556	15.433	15.667	29901133	4.11	5315403	3.17	5.63	V	
22	16.830	16.642	16.975	28092451	3.86	4691315	2.80	5.99		
23	17.838	17.692	17.908	42767870	5.87	6544285	3.90	6.54	V	
24	18.140	18.083	18.208	16456113	2.26	4279476	2.55	3.85	V	
25	20.718	20.458	20.883	110052871	15.11	11646682	6.94	9.45		
26	20.957	20.883	21.117	24919311	3.42	5173756	3.08	4.82	V	
27	21.167	21.117	21.225	5359607	0.74	1973915	1.18	2.72	V	
28	21.478	21.400	21.567	7080699	0.97	1708005	1.02	4.15		
				728298591	100.00	167790709	100.00			

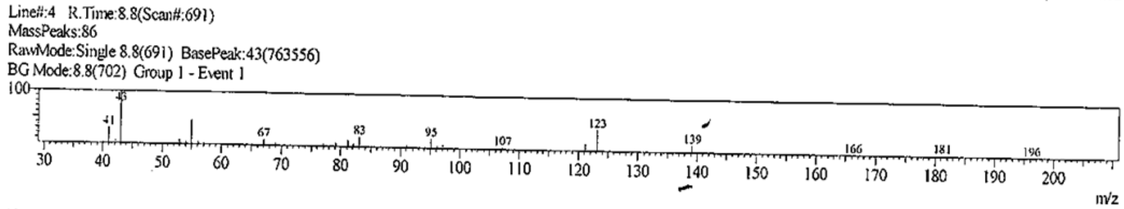
Spectrum

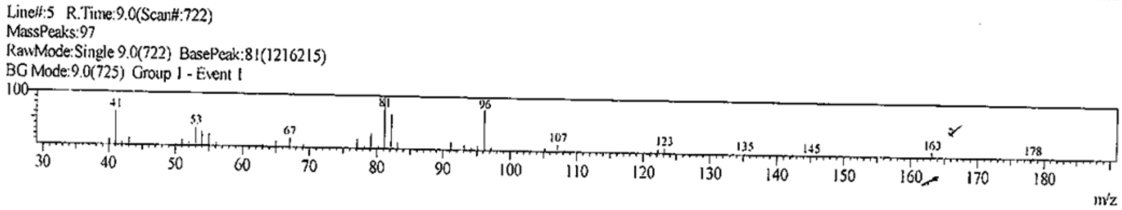
Line#:1 R.Time:3.1(Scan#:8)
MassPeaks:53
RawMode:Single 3.1(8) BasePeak:47(105072)
BG Mode:3.0(4) Group 1 - Event 1

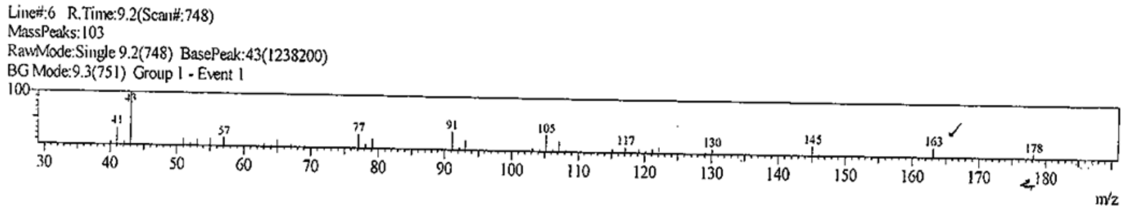


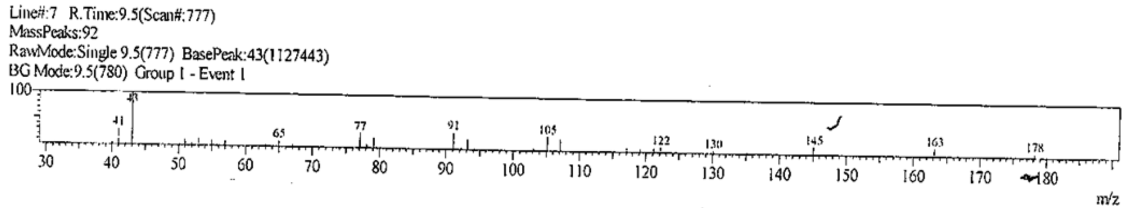

Line#:2 R.Time:5.9(Scan#:352)
MassPeaks:69
RawMode:Single 5.9(352) BasePeak:82(6397887)
BG Mode:6.0(363) Group 1 - Event 1

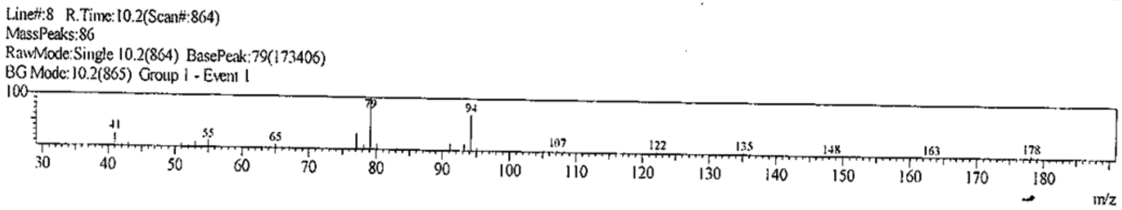

Line#:3 R.Time:8.1(Scan#:608)
MassPeaks:87
RawMode:Single 8.1(608) BasePeak:79(157344)
BG Mode:8.1(610) Group 1 - Event 1

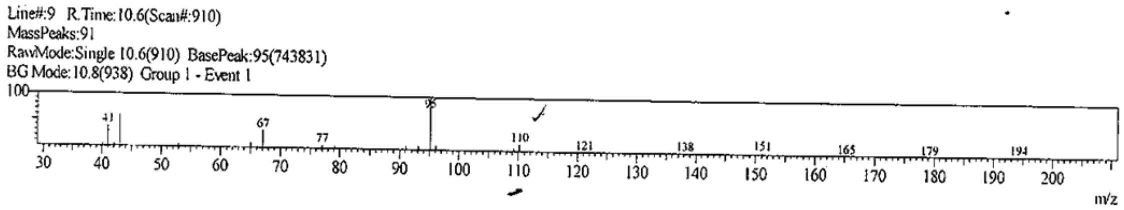

Line#:4 R.Time:8.8(Scan#:691)
MassPeaks:86
RawMode:Single 8.8(691) BasePeak:43(763556)
BG Mode:8.8(702) Group 1 - Event 1


Line#:5 R.Time:9.0(Scan#:722)
MassPeaks:97
RawMode:Single 9.0(722) BasePeak:81(1216215)
BG Mode:9.0(725) Group 1 - Event 1

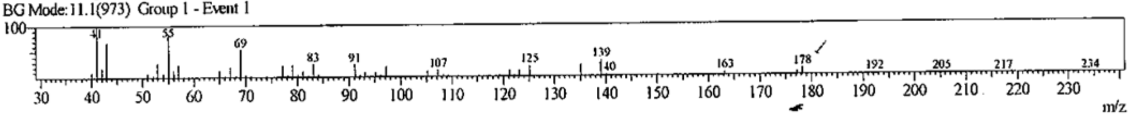

Line#:6 R.Time:9.2(Scan#:748)
MassPeaks:103
RawMode:Single 9.2(748) BasePeak:43(1238200)
BG Mode:9.3(751) Group 1 - Event 1


Line#:7 R.Time:9.5(Scan#:777)
MassPeaks:92
RawMode:Single 9.5(777) BasePeak:43(1127443)
BG Mode:9.5(780) Group 1 - Event 1

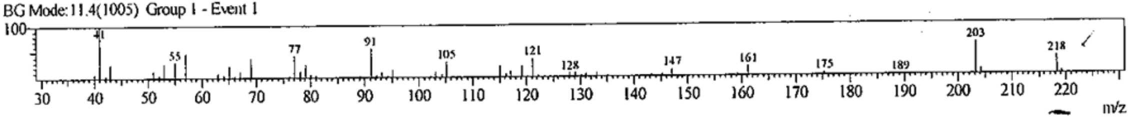

Line#:8 R.Time:10.2(Scan#:864)
MassPeaks:86
RawMode:Single 10.2(864) BasePeak:79(173406)
BG Mode:10.2(865) Group 1 - Event 1


Line#:9 R.Time:10.6(Scan#:910)
MassPeaks:91
RawMode:Single 10.6(910) BasePeak:95(743831)
BG Mode:10.8(938) Group 1 - Event 1

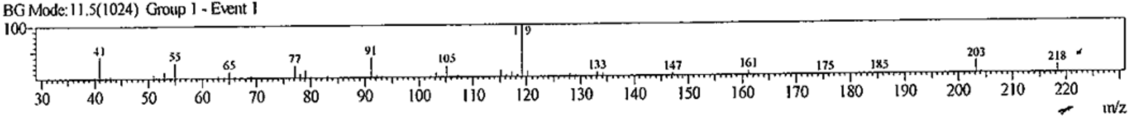
Line#:10 R.Time:11.1(Scan#:977)
MassPeaks:134
RawMode:Single 11.1(977) BasePeak:41(419553)
BG Mode:11.1(973) Group 1 - Event 1



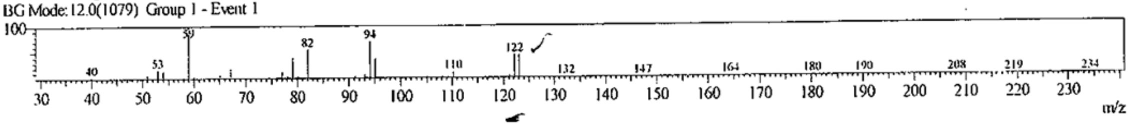
Line#:11 R.Time:11.3(Scan#:1001)
MassPeaks:117
RawMode:Single 11.3(1001) BasePeak:41(451826)
BG Mode:11.4(1005) Group 1 - Event 1



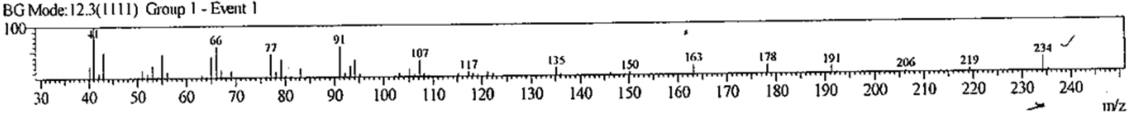
Line#:12 R.Time:11.6(Scan#:1028)
MassPeaks:115
RawMode:Single 11.6(1028) BasePeak:119(732133)
BG Mode:11.5(1024) Group 1 - Event 1



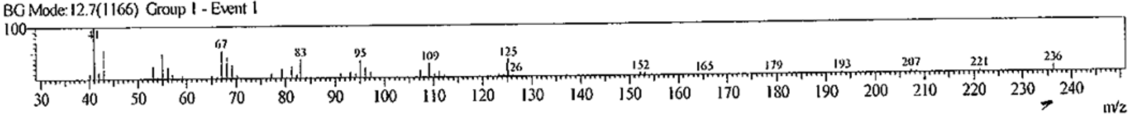
Line#:13 R.Time:12.0(Scan#:1080)
MassPeaks:74
RawMode:Single 12.0(1080) BasePeak:59(84022)
BG Mode:12.0(1079) Group 1 - Event 1



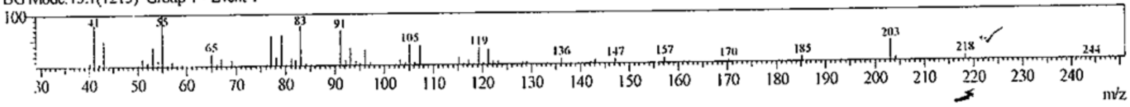
Line#:14 R.Time:12.4(Scan#:1126)
MassPeaks:135
RawMode:Single 12.4(1126) BasePeak:41(430299)
BG Mode:12.3(1111) Group 1 - Event 1



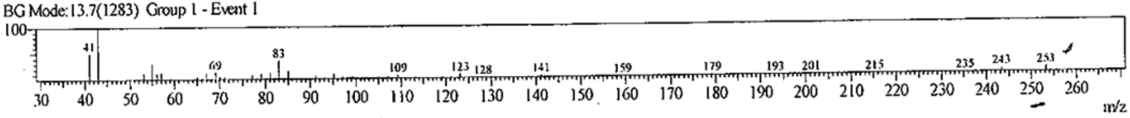
Line#:15 R.Time:12.6(Scan#:1148)
MassPeaks:100
RawMode:Single 12.6(1148) BasePeak:41(317547)
BG Mode:12.7(1166) Group 1 - Event 1



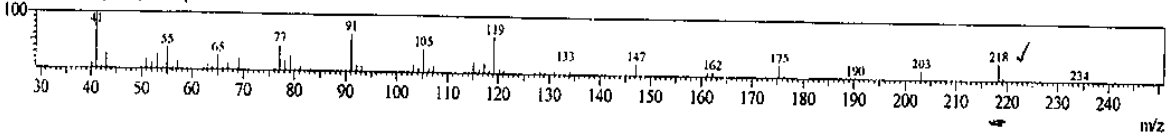
Line#:16 R.Time:13.2(Scan#:1220)
MassPeaks:133
RawMode:Single 13.2(1220) BasePeak:55(178677)
BG Mode:13.1(1213) Group 1 - Event 1



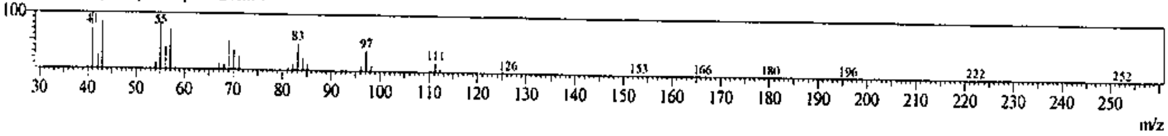
Line#:17 R.Time:13.5(Scan#:1264)
MassPeaks:193
RawMode:Single 13.5(1264) BasePeak:43(806463)
BG Mode:13.7(1283) Group 1 - Event 1



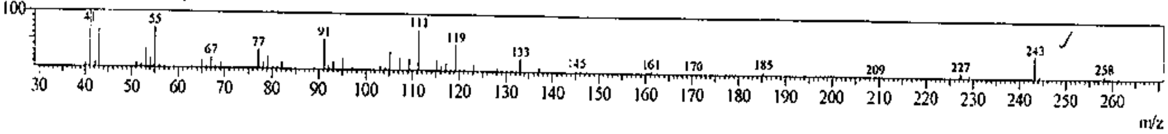
Line#:18 R.Time:13.9(Scan#:1303)
MassPeaks:125
RawMode:Single 13.9(1303) BasePeak:41(709021)
BG Mode:14.1(1331) Group 1 - Event 1



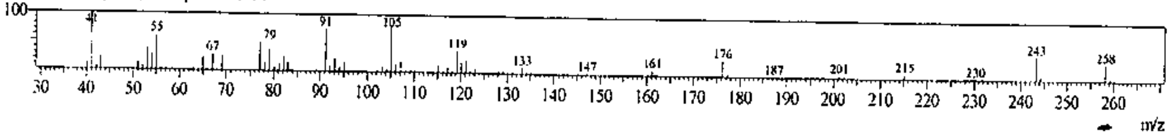
Line#:19 R.Time:14.5(Scan#:1375)
MassPeaks:80
RawMode:Single 14.5(1375) BasePeak:41(281674)
BG Mode:14.4(1373) Group 1 - Event 1



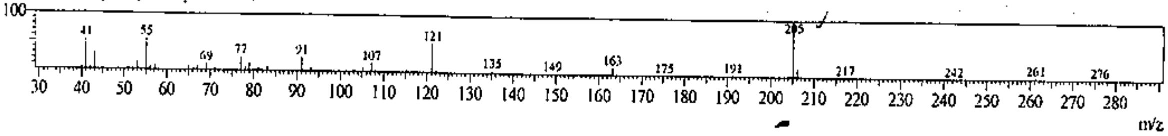
Line#:20 R.Time:14.9(Scan#:1430)
MassPeaks:136
RawMode:Single 14.9(1430) BasePeak:41(35666)
BG Mode:14.9(1429) Group 1 - Event 1



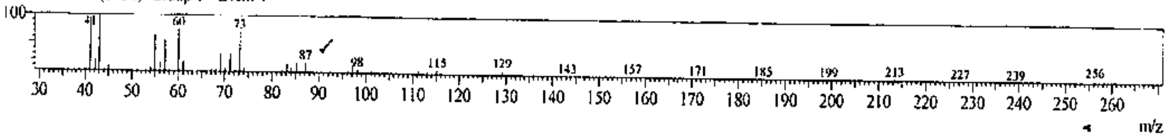
Line#:21 R.Time:15.6(Scan#:1508)
MassPeaks:152
RawMode:Single 15.6(1508) BasePeak:41(385253)
BG Mode:15.6(1518) Group 1 - Event 1



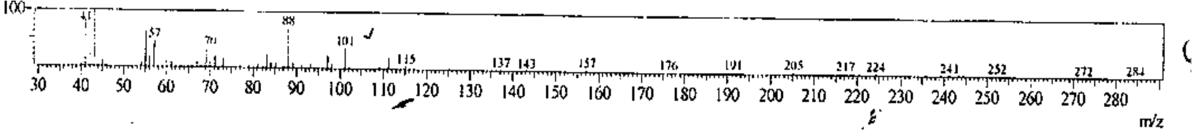
Line#:22 R.Time:16.8(Scan#:1661)
MassPeaks:126
RawMode:Single 16.8(1661) BasePeak:205(698107)
BG Mode:17.1(1690) Group 1 - Event 1



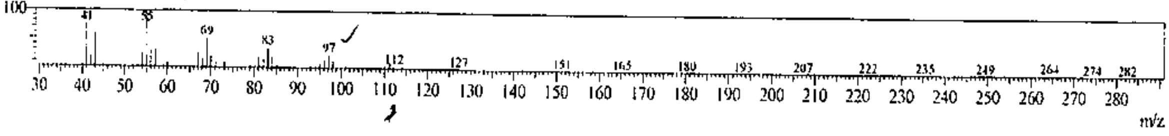
Line#:23 R.Time:17.8(Scan#:1781)
MassPeaks:94
RawMode:Single 17.8(1781) BasePeak:43(286238)
BG Mode:17.9(1784) Group 1 - Event 1

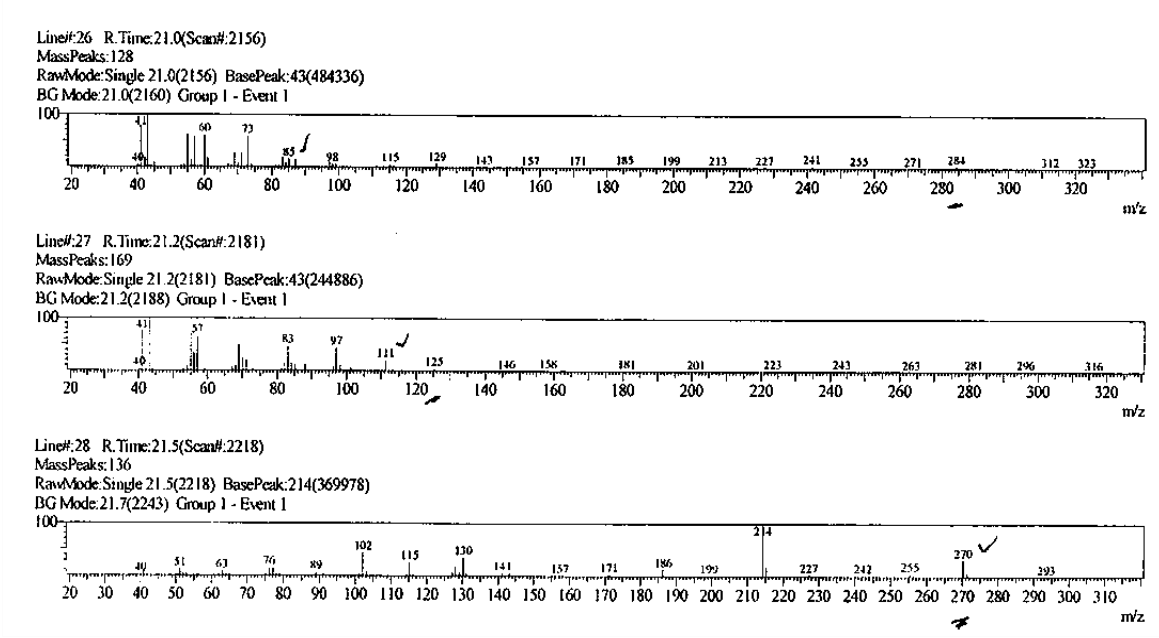


Line#:24 R.Time:18.1(Scan#:1818)
MassPeaks:133
RawMode:Single 18.1(1818) BasePeak:43(41346)
BG Mode:18.2(1819) Group 1 - Event 1



Line#:25 R.Time:20.7(Scan#:2127)
MassPeaks:140
RawMode:Single 20.7(2127) BasePeak:55(951322)
BG Mode:20.8(2133) Group 1 - Event 1





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