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# BIOCRUDES FROM HYDROCARBON PLANTATION AS A RENEWABLE SOURCE FOR FUELS

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## ABSTRACT

The present investigation, which is a continuation of previous work in our laboratory, deals with the preparation of biocrudes from latex-producing plants. The plants considered here are mainly*Euphorbia geniculata*and *Euphorbia pseudograntii*of the family *Euphorbiaceae* which grow in the arid and/or semi-arid areas. Soxhlet extractions of the dry powder of these plants using different polarity solvents: petroleum ether 60-80$^0$C,cyclohexane, benzene or ethanol give,in general, exceptionally high yields of biocrudes compared with the other latex-producing plants. These solvents are used either separately or consecutively. The highest yield ever of biocrude (17.2%) is obtained with *Euphorbia geniculata* using ethanol as a solvent.

The extracted biocrudes are characterized with very low sulfur contents in the range of 0.01 to 0.04% and low nitrogen contents in the range of 0.2 to 1.2%. The fuels obtained after conversion of these biocrudes are considered,therefore, environmentally friendly. Furthermore, their average molecular weights in the range of300 to 984 are most suitable for the conversion to different yields of fuels boiling in the ranges of gasoline, kerosene or gas oil.

FT-IR measurements of the obtained biocrudesindicate that their main structures are multi cyclohexyl ring systems with side chains having different functional groups such as hydroxyl, ester and unsaturation positions.

## 1. INTRODUCTION

Extensive arid and semi-arid areas could be cultivated with certain types of latex-producing plants. These plants require no fertilization and depend on the minimum amounts of rain, underground water or sewage water. The latex obtained from such plants constitutes a rich renewable source for biocrudes which after conversion to hydrocarbons yield a spectrum of biofuels. Such hydrocarbon plantation trend is considered one of the promising approaches and solutions to the problem of the fast depletion of petroleum reserves [1-4].

In this respect, research around the world has identified specific plant families capable of supplementing or replacing current petroleum derived fuels through their latexes.

Melvin Calvin in 1978 has introduced some latex-producing plants from diverse families including Euphorbiaceae, Asclepideaceae and Moraceae[5]. Calvin and co-workers have proposed a search for plant species that generate a high proportion of hydrocarbon-like constituents [6]. Buchanan and associates summarized a number of plant species that fulfill these requirements [7]. These latex-producing plants are highly interesting also because their molecular structure including carbon numbers of $C_{15}$, $C_{20}$, $C_{30}$ are most suitable for the conversion to liquid fuels similar to petroleum.

Hydrocarbon producing plants are fully-grown in less than one year, thereafter producing latex and thence biocrude for unlimited years. Hydrocarbon plantation is also economically feasible as indicated by several international studies [8-9].

## 2. EXPERIMENTAL

### Materials

#### *Chemicals*

Chemicals used throughout this investigation including ethanol, benzene, cyclohexane and petroleum ether 60-80$^0$C were analytical gradeexcept ethanol (pure grade). These chemicals were supplied by El-Nasr for Chemicals Co., Cairo, Egypt.

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***Plant material***

*Euphorbia geniculata* and *Euphorbia pseudograntii* plants were both grown in the ground of the Egyptian Petroleum Research Institute **Figures (1-2)**. Fresh sample of these plants were shredded with a razor blade and then dried at 80$^0$C for 33 hrs until constant weight was reached. By a milling machine, the dried plant sample was grinded to produce fine powder. The milled samples were mixed carefully and stored in a glass bottle at room temperature for subsequent uses.

***Preparation of extract***

Powdered homogeneous dried plant (40 gm) was settled in a Soxhlet extractor (2 liter capacity). Then 1500 ml of each of the different polarity solvents namely ethanol, benzene, cyclohexane and petroleum ether 60-80$^0$C were added in the flask of the extraction system. These solvents were previously dried with anhydrous sodium sulphate over night. The extractions were carried out on the different parts of each plant including the leaves and stems in addition to the whole plant. After the extraction period, the solvents were removed under vacuum with rotary evaporator until a constant weight of extracted biocrude was reached.

**Methods of Analysis**

***Chemical Analysis Methods***

**Elemental analysis Method**

Carbon, hydrogen, and nitrogen (weight percent) of the extracted samples were carried out at the Microanalysis Laboratory of Cairo University, Giza, Egypt. The sulfur content was determined by ASTM-D129 method on X-Ray unit at the Evaluation Department of the Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo, Egypt.

**Average molecular weight determination**

The average molecular weights of the extracted samples, determined by the freezing point depression method of benzene, were carried out at the Evaluation Department of EPRI, Nasr City, Cairo, Egypt.

***Spectral Analysis Methods***

**Infra-red Absorption Spectroscopy (FT-IR)**

The qualitative infrared absorption spectra of the extracted biocrudes were recorded on Nicolet IS-10 FT-IR (Code: Cs-Q-01), using KBr as a dispersion medium at the Evaluation Department of EPRI. The recorded spectra were investigated and the band assignments of the different groups were made by simple inspection and referenced to generalized charts of the characteristic group frequencies [9]. A spectrum was scanned between (4000-400cm$^{-1}$).

## 3. RESULTS AND DISCUSSION

**General extraction procedure (Soxhlet extraction)**

In this investigation, the two latex-bearing plants namely, *Euphorbia geniculata* and *Euphorbia pseudograntii* are utilized as a sustainable energy source for producing biofuels. These plants which grow in the arid and/or semi-arid areas without fertilization do not compete with food crops or fiber crops. It is worthwhile to mention that these plants store carbon in their latex in the form of hydrocarbon emulsion.

Pulverized dry samples (40gm) of each of *Euphorbia geniculata* and *Euphorbia pseudograntii* yield biocrudes after extraction in a Soxhlet for a continuous period of 8hr using petroleum ether, cyclohexane, benzene or ethanol as solvents. Yields, elemental analyses and average molecular weights of the extracted samples are presented in **Table 1**.

Another sample of the pulverized plant *Euphorbia geniculata* (40gm) is extracted consecutively with petroleum ether (8hrs reflux) to yield 4.7 gm extract followed by benzene (8hrs reflux) to yield 1.3 gm extract and finally ethanol (8hrs reflux) to yield 4.8 gm extract according to this increasing order of solvent polarity. The same was applied for *Euphorbia pseudograntii*. Yields, elemental analyses and average molecular weights of the extracted samples using these different polarity solvents are presented in **Table 2**.

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It is worth noting that ethanol is the most efficient extracting solvent. This may be due to the fact that ethanol with its high polarity is capable of extracting non-polar hydrocarbons, semi-polar and other polar components including alcohols, esters and oxygenated natural derivatives. It is also apparent that petroleum ether is slightly more efficient due to extracting more of the non-polar paraffinic hydrocarbons.

Other samples of the dried plants (40gm each) are extracted with benzene (16hrs and 32hrs) to yield 5.8 gm and 7.0 gm with *Euphorbia geniculata* compared to 4.9 gm and 5.2 gm with *Euphorbia pseudograntii*, respectively. It may be pointed out that the yield of the extracted biocrude increases with increasing the extraction time up to 32hrs using the same solvent. Yields, elemental analyses and average molecular weights of the extracted samples using benzene as a solvent are presented in **Table 3**.

Extractions of plant materials including the dried leaves, stems or the whole plants are carried out for comparison using petroleum ether as a solvent. It may be noted that the extract yield of biocrude of the leaves are considerably higher than the corresponding stems and the whole plants. Yields, elemental analyses and average molecular weights of the extracted samples using petroleum ether are presented in **Table 4**.

From the presented data in **Tables (1-4)**, we note that the hydrogen to carbon ratios (H/C) of the extracted biocrudes are almost in the range of that of hydrocarbon fuels which mainly contain hydrocarbons with very low percentages of sulfur and nitrogen indicating that the fuels obtained from their conversion is environmentally friendly [10-11]. These biocrudes are highly interesting also because their average molecular weights are suitable for the conversion to liquid fuels in the ranges of gasoline, kerosene and gas oil similar to petroleum.

**Characterization of biocrude extracts of the cultivated latex-producing plants I, II.**

**Figure 3**shows the IR-spectrum of different polarity solvent extracts of biocrudes obtained from *Euphorbia geniculata* (I). The spectrum of all solvent extracts shows a broad absorption band at (3440-3320cm$^{-1}$) for O-H stretching. The spectrum also shows C-H stretching vibrations at (2924-2850 cm$^{-1}$) for asymmetric and symmetric stretching cycloalkyl skeleton bearing alkyl group. The absorption band at (1741-1728cm$^{-1}$) is assignable to C=O stretch of ester and a band at (1462-1376cm$^{-1}$) is assignable to methyl asymmetric and methyl symmetric C-H bending vibration. The absorption band at (1263-1236cm$^{-1}$) is the C-H symmetric of alkene. A set of methylene group-$(CH_2)_n$- in the side chain appears as a weak band at (724-720cm$^{-1}$). Except petroleum ether, benzene and cyclohexane extract from (I) showed another band at (1650-1603cm$^{-1}$) for C=C stretching. Similarly the biocrude was analyzed by FTIR in *Euphorbia antisyphilitica*and *Euphorbia rigida*[12-13].This likewise in plant (II) but the petroleum ether, cyclohexane and ethanol extract only showed unsaturation position C=C stretching. **Figure 4**.

**Figure 5**shows the IR-spectrum of petroleum ether (60-80%) solvent extract of biocrude obtained from different parts of the cultivated plants like leaves, stems and the whole of plant. All spectrums of solvent extracts show a broad absorption band at (3428-3357cm$^{-1}$) for O-H stretching. The spectrum also shows C-H stretching vibrations at (2934-2850cm$^{-1}$) for asymmetric and symmetric stretching cycloalkyl skeleton bearing alkyl group. The absorption band at (1742-1736cm$^{-1}$) is assignable to C=O stretch of ester and a band at (1454-1384cm$^{-1}$) is assignable to methyl asymmetric and methyl symmetric C-H bending vibration. The absorption band at (1260-1236cm$^{-1}$) is the C-H symmetric of alkene. A set of methylene group-$(CH_2)_n$- in the side chain appears as a weak band at (724-722cm$^{-1}$). Except the leaves and whole plant extracts of *Euphorbia geniculata* (I)showed unsaturation band at (1635-1603cm$^{-1}$) for C=C stretching. Furthermore, except the leaves of *Euphorbia pseudograntii* (II) showed unsaturation position at (1603cm$^{-1}$) **Figure 6.**

**Figure 7**Shows the IR-spectrum of benzene solvent extract of the cultivated plants (I) by different time of extraction period 8, 16 and 32hrs. All spectrums of solvent extracts show a broad absorption band at (3441-3368cm$^{-1}$) for O-H stretching. The spectrum also shows C-H stretching vibrations at (2934-2850cm$^{-1}$) for asymmetric and symmetric stretching cycloalkyl skeleton bearing alkyl group. The absorption band at (1741-1731cm$^{-1}$) is assignable to C=O stretch of ester and a band at (1461-1376cm$^{-1}$) is assignable to methyl asymmetric and methyl symmetric C-H bending vibration. The absorption band at (1263-1237cm$^{-1}$) is the C-H symmetric of alkene. A set of methylene group-$(CH_2)_n$- in the side chain appears as a weak band at (724-700cm$^{-1}$). This is likewise in the cultivated plant (II) **Figure 8**.

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**Figures (7-8)** indicates that the intensity of OH band increased with increasing the extraction time, probably due to the hydration of the double bond which explains the disappearance of the unsaturation band.

The measured FT-IR spectra given in **Figures (3-8)**, show clearly the CH- stretching vibration for asymmetric and symmetric cyclohexyl skeleton bearing alkyl groups and the presence of CH- symmetric of alkene along with bands of methylene and methyl groups in the side chain. This confirms the hydrocarbon nature of the multi-ring systems characteristic of the biocrude. These findings coincide with the published data that these main structures correspond to terpenes derivatives [14].

## 4. CONCLUSIONS

From the experimental results, *Euphorbia geniculata* and *Euphorbia pseudograntii* of the family *Euphorbiaceae*can be considered as a potential source of biocrude producing environmentally friendly renewable hydrocarbon fuels. These latex producing plants, which grow in the arid or semi-arid areas, do not compete with food crops or fiber crops. A definite advantage to be recorded also is the highest yield ever reported of biocrude (17.2%) obtained from Euphorbia geniculata using ethanol as a solvent. Furthermore, IR spectra indicate multi cyclic ring structures with side chains characteristic of the biocrude.These advantages encourage the use of Latex-producing plants as a sustainable energy source for fuels.

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***Table (1)Separately Soxhlet extractions of Euphorbia geniculata (I) and Euphorbia pseudograntii (II) latex-producing plants (8hrs) using different polarity solvents. (Feed: 40 gm dry sample)***

| Solvent | Plant | Yield | | Elemental analysis wt% | | | | Average molecular weight |
|---|---|---|---|---|---|---|---|---|
| | | Gm | % | C | H | S | N | |
| Petroleum ether(60-80$^0$c) | I | 4.7 | 11.7 | 78.8 | 11.1 | 0.04 | 0.2 | 570 |
| | II | 3.8 | 9.5 | 72.0 | 11.5 | 0.01 | 0.2 | 671 |
| Cyclohexane | I | 5.0 | 12.5 | 74.6 | 10.7 | 0.03 | 0.4 | 446 |
| | II | 4.2 | 10.5 | 74.8 | 10.8 | 0.02 | 0.3 | 473 |
| Benzene | I | 5.4 | 13.5 | 73.7 | 9.4 | 0.04 | 0.5 | 785 |
| | II | 4.7 | 11.7 | 75.6 | 11.7 | 0.04 | 0.3 | 876 |
| Ethanol | I | 6.9 | 17.2 | 53.3 | 8.5 | 0.02 | 1.6 | 423 |
| | II | 6.2 | 15.5 | 48.1 | 9.3 | 0.05 | 0.8 | 300 |

***Table (2)Consecutively Soxhlet extractions of Euphorbia geniculata (I) and Euphorbia pseudograntii (II) latex-producing plants (8hr) using different polarity solvents. (Feed: 40 gm dry sample)***

| Solvent | Plant | Yield | | Elemental analysis wt% | | | | Average molecular weight |
|---|---|---|---|---|---|---|---|---|
| | | Gm | % | C | H | S | N | |
| Petroleum ether | I | 4.7 | 11.7 | 78.8 | 11.1 | 0.04 | 0.2 | 570 |
| | II | 3.8 | 9.5 | 72.0 | 11.5 | 0.01 | 0.2 | 671 |
| Benzene | I | 1.3 | 3.2 | 71.9 | 10.2 | 0.07 | 0.6 | 626 |
| | II | 1.5 | 3.7 | 72.0 | 10.2 | 0.05 | 0.7 | 552 |
| Ethanol | I | 4.8 | 12.0 | 48.2 | 7.3 | 0.03 | 1.2 | 434 |
| | II | 3.4 | 8.5 | 43.9 | 7.0 | 0.07 | 1.4 | 312 |

***Table (3)Soxhlet extractions of Euphorbia geniculata (I) and Euphorbia pseudograntii (II) latex-producing plants using benzene by different extraction times. (Feed: 40 gm dry sample)***

| Time of extraction | Plant | Yield | | Elemental analysis wt% | | | | Average molecular weight |
|---|---|---|---|---|---|---|---|---|
| | | Gm | % | C | H | S | N | |
| 8hr | I | 5.4 | 13.5 | 73.7 | 9.4 | 0.04 | 0.5 | 785 |
| | II | 4.7 | 11.7 | 75.6 | 11.7 | 0.04 | 0.3 | 876 |
| 16hr | I | 5.8 | 14.5 | 73.0 | 10.1 | 0.02 | 0.5 | 984 |
| | II | 4.9 | 12.2 | 74.7 | 10.0 | 0.01 | 0.4 | 964 |
| 32hr | I | 7.0 | 17.5 | 75.1 | 10.0 | 0.03 | 0.3 | 890 |
| | II | 5.2 | 13.0 | 74.0 | 8.3 | 0.02 | 0.2 | 691 |

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*Table (4)Soxhlet extractions of different parts of Euphorbia geniculata (I) and Euphorbia pseudograntii (II) latex-producing plants (8hr) using petroleum ether (60-80$^0$C). (Feed: 40 gm dry sample)*

| Extracted Part | Plant | Yield | | Elemental analysis wt% | | | | Average molecular weight |
|---|---|---|---|---|---|---|---|---|
| | | Gm | % | C | H | S | N | |
| Leaves | I | 4.7 | 11.7 | 78.8 | 11.1 | 0.04 | 0.2 | 570 |
| | II | 3.8 | 9.5 | 72.0 | 11.5 | 0.01 | 0.2 | 671 |
| Stems | I | 2.0 | 5.0 | 75.0 | 10.5 | 0.03 | 0.3 | 594 |
| | II | 2.6 | 6.5 | 84.4 | 11.9 | 0.03 | 0.2 | 914 |
| Whole plant | I | 3.6 | 9.0 | 74.6 | 10.0 | 0.02 | 0.2 | 550 |
| | II | 2.8 | 7.0 | 72.0 | 10.3 | 0.02 | 0.1 | 582 |

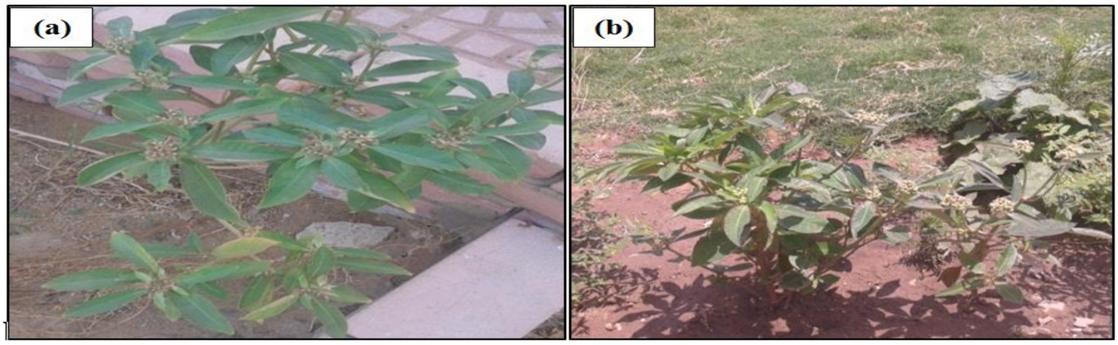


*Figure 1. (a) A three- month old shrub of Euphorbia geniculata, (b) A six- month old shrub of Euphorbia geniculata*

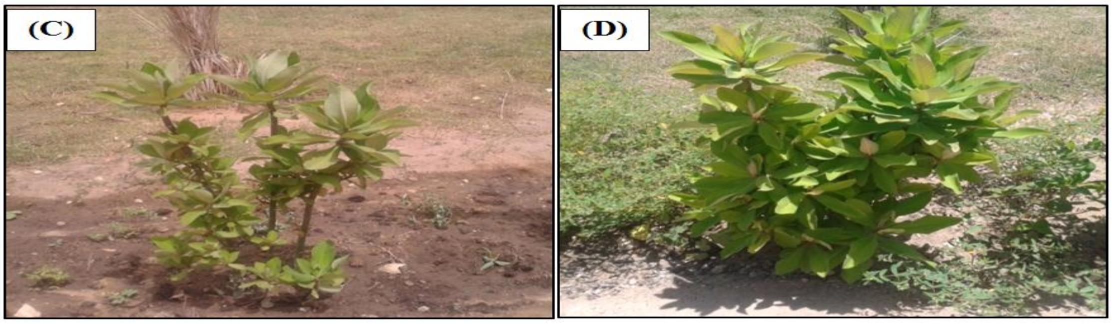


*Figure 2.(C)A four- month old shrub of Euphorbia pseudograntii, (D) One - year old shrub of Euphorbia pseudograntii*

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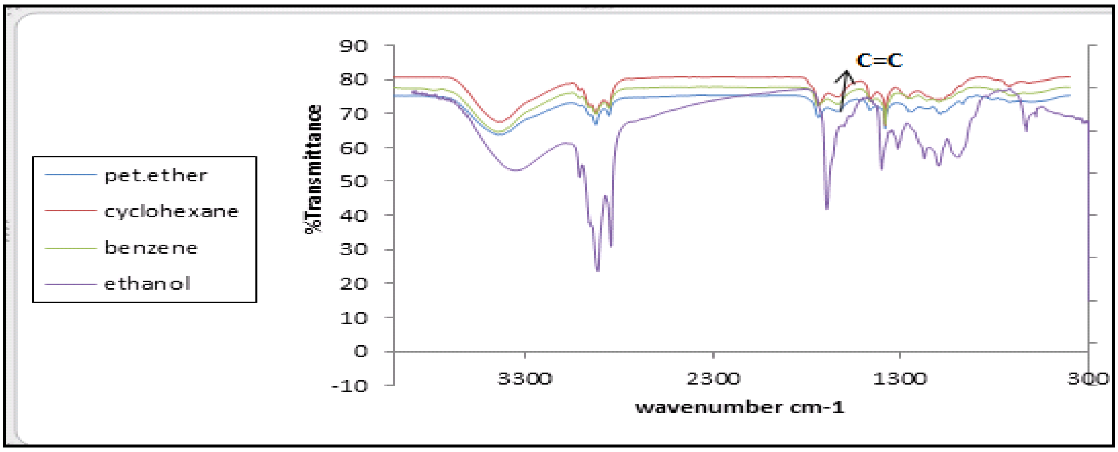


*Figure 3. FT-IR spectrum of all solvent extract of Euphorbia geniculata*

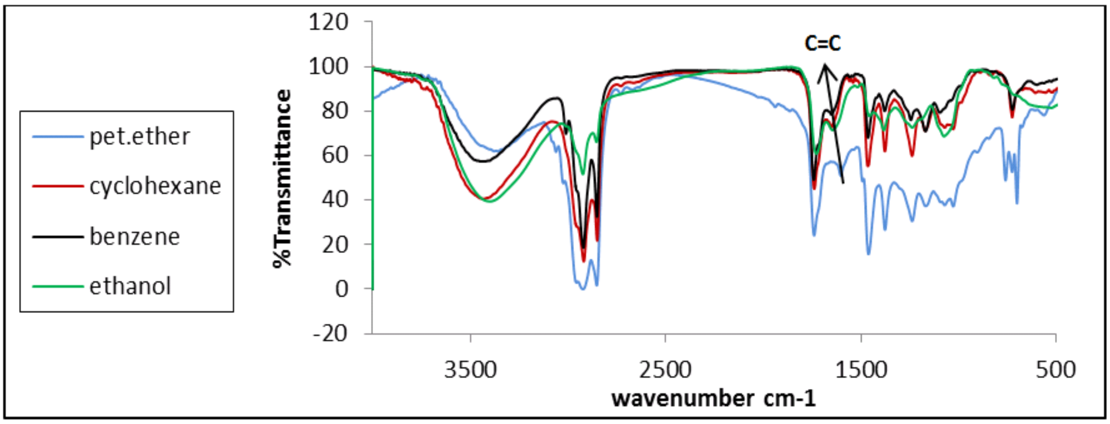


*Figure 4. FT-IR spectrum of all solvent extract of Euphorbia pseudograntii*

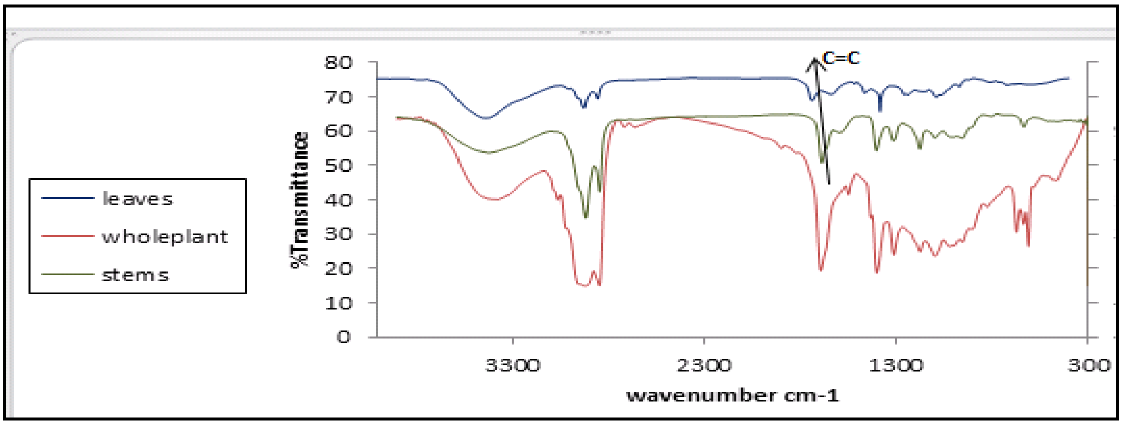


*Figure 5. FT-IR spectrum of petroleum ether (60-80%) solvent extract obtained from different parts of Euphorbia geniculata*

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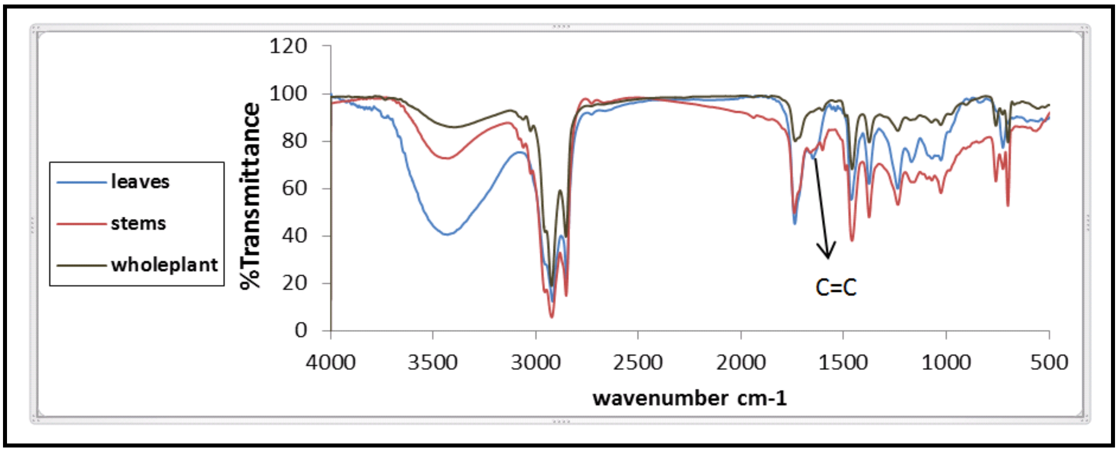


*Figure 6. FT-IR spectrum of petroleum ether (60-80%) solvent extract obtained from different parts of Euphorbia pseudograntii*

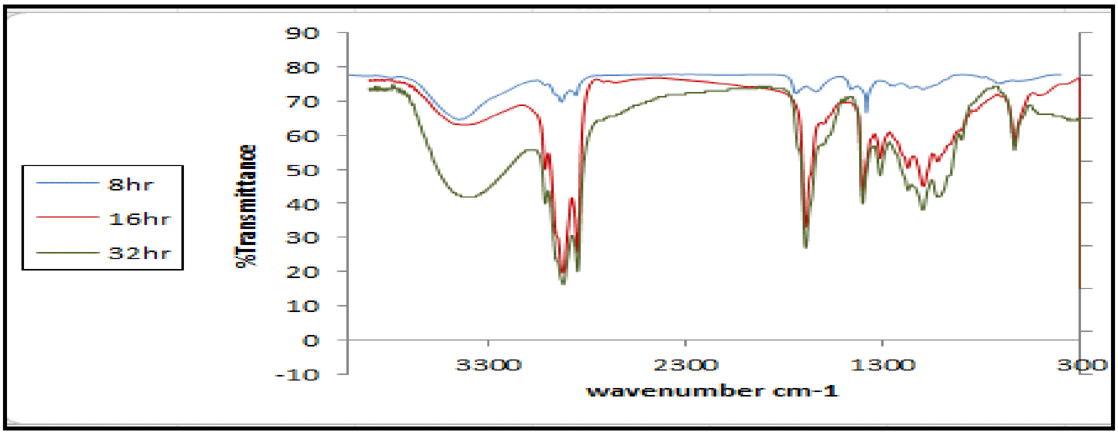


*Figure 7.FT-IR spectrum of benzene solvent extract obtained from different time extraction of Euphorbia geniculata*

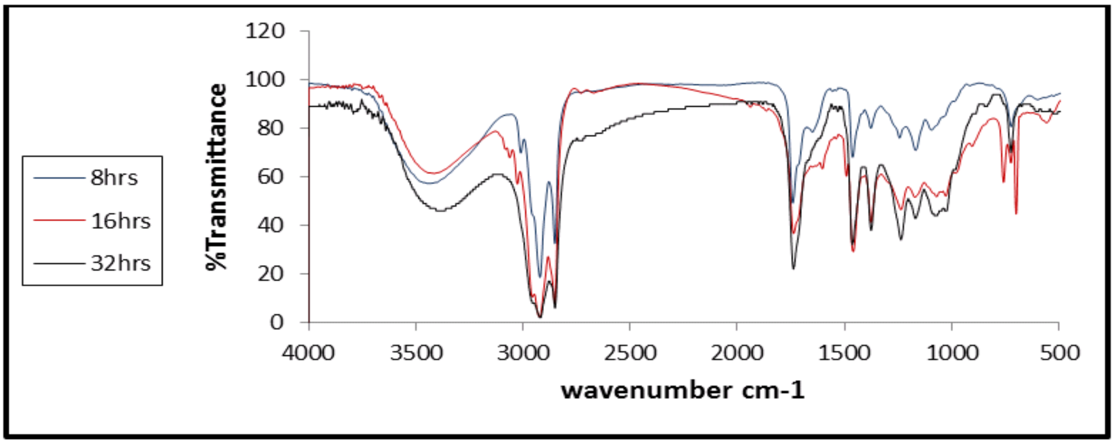


*Figure 8. FT-IR spectrum of benzene solvent extract obtained from different time extraction of Euphorbia pseudograntii*