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Analytical and Spectral Studies on Multi-use Hydrocarbanaceous Plant Species of Western Ghats, Tamil Nadu, India

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Large-scale screening of plants growing in the Western Ghats, Tamil Nadu, India was conducted to assess the hydrocarbon production and the type of isoprene compound(s) present. Three species contained more than 3% hydrocarbon. *Sarcostemma brevistigma* had the highest concentration of hydrocarbon with 3.6%. Seven species contained more than 2% of hydrocarbons amount the plant species screened. The hydrocarbon fraction of *Ficus elastica* (leaf) had a gross calorific value of 9834 cal/g (41.17 MJ/kg), which is close to the calorific value of fuel oil. Six-hydrocarbon fraction contained gross calorific value of more than 9000 cal/g (37.68 MJ/kg). Of the 13 species hydrocarbon fraction analyzed, seven species contained *cis*-polyisoprene compounds, while two species contained *trans*-polyisoprenes. *Cis* and *trans* polyisoprenes are potential alternative energy sources for fuel and/or as industrial raw materials.

Key Words: Analytical, Spectral, Hydrocarbonaceous plants, Western Ghats, Tamil Nadu.

INTRODUCTION

The exponential growth in the number of people, increases in the number of automobiles and vehicles and the sophistication of technology has increased an awareness of the need to discover new energy sources from diverse under-utilized plant species. There is little doubt that petroleum cannot be indefinitely relied upon as a stable economical raw material to satisfy energy and industrial feed stock needs. The shortage and depletion of petroleum have led us to the search for alternative sources of fuels and chemicals.

Hydrocarbons in plants, such as natural rubber (polyisoprene) have chemical structures similar to many hydrocarbons derived from petroleum (m.w. 10,000), but with molecular weights in the order of 500,000 to 2,000,000. Such materials when cracked will produce hydrocarbons of lower molecular weight, which can be used as alternative energy sources for fuel and/or chemical raw materials that are used in the manufacturing of a large number of products[1].

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Plants as a source of hydrocarbons and rubber have been investigated periodically for many years[1-4]. During World War II, there was an increased effort in search of rubber producing plants. However, during the last few decades the need for additional sources has resurfaced, since the world production of natural rubber is expected to be insufficient for the demand[3]. Our main objective was to do a large-scale screening of plants growing in the Western Ghats region to assess their hydrocarbon production and the type of isoprene compounds present.

EXPERIMENTAL

Healthy plant samples belonging to same agro-climatic zone were randomly collected from a minimum of 20–25 populations with 15–20 plants per population to obtain a sample with a fresh weight of 2000–2500 g and composited into one sample for chemical analysis. Each sample was sub-sampled twice. Plant samples of 46 species belonging to various families were collected from Courtallum to Srivilliputhur (RF) of the Western Ghats, Tamil Nadu, India for analysis. When collecting samples, herbaceous and small woody plants were clipped at ground level after completion of the seasonal growth and for large woody plants, only the recent growth was removed. Whole plant samples (stems, leaves, fruits and seeds) were analyzed for chemical composition. Plant materials were chopped into small pieces, allowed to dry in a sheltered area at ambient temperature ranging from 10 to 30°C and then ground in a Wiley mill with a 1 mm sieve.

The hydrocarbon fraction was removed from samples using hexane in a Soxhlet apparatus for 24 h. After hexane removal, the hydrocarbon fractions were dried and weighed for yield[2].

NMR spectra of hydrocarbon samples were obtained using a Bruker (300 MHz) AC 300F NMR spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. *Cis*-methyl was observed at 1.64 ppm and *trans*-methyl at 1.53 ppm. The methylene resonance appears near 2.1 and 2.03 ppm, respectively, for the *cis* and *trans*. The position of vinylene proton resonance is insensitive to the geometrical isomerism about the double bond appearing at 5.2 ppm for both the *cis* and *trans* systems. The most useful resonances for analytical purposes are the methyl peaks at 1.59 ppm for the 3,4 units and 1.05 ppm for the 1,2 units[5, 6]. Gross calorific value of hydrocarbon fraction was determined by Bomb calorimeter (Toshniwal, model cc. 0.1)[7].

Three replications of each sample were used for extraction of hydrocarbon fraction. Values in Table-1 are the means of three replications, with the standard deviation (±S.D.).

RESULTS AND DISCUSSION

Hydrocarbon: All the plant species screened were shrubs, climbers, woody climbers, tree suitable for annual pollarding with potential fibre utility except for *Caralluma attenuata, Euphorbia hirta, E. heterophylla* and *Croton sparsiflorus* which were herbs.

TABLE-1
PLANT SPECIES FROM THE WESTERN GHATS, INDIA, CONTAINING 1.5% OR MORE HYDROCARBONS

Name of the plant species	Family	Yield of hydrocarbon (%)*	Nature of hydrocarbon	Gross calorific value cal/g (MJ/kg)	
Sarcostemma brevistigma W. and A.	Asclepiadaceae	3.6 ± 0.27	*Trans* methyl with 1,2 + 3,4 moieties + methylene nearly *trans*	8733.0 ± 10.1	(36.563 ± 0.042)
Caralluma attenuata Wt.	Asclepiadaceae	3.4 ± 0.28	*Cis* methyl with 1,2 + 3,4 moieties + methylene nearly *trans*	9292.3 ± 38.3	(38.905 ± 0.160)
Jatropha multifida L.	Euphorbiaceae	3.0 ± 0.16	Methyl 1,2 + 3,4 moieties + methylene nearly *trans*	8821.0 ± 20.5	(36.932 ± 0.085)
Tylophora asthmatica W. and A.	Asclepiadaceae	2.7 ± 0.29	*Cis* methyl with 1,2 + 3,4 moieties + methylene nearly *trans*	9378.0 ± 35.1	(39.264 ± 0.147)
Euphorbia tirucalli. L.	Euphorbiaceae	2.6 ± 0.16	*Cis, trans* methyl with 1,2 + 3,4 moieties + methylene nearly *trans*	7832.1 ± 22.7	(32.791 ± 0.095)
Cryptostegia grandiflora R.Br.	Asclepiadaceae	2.3 ± 0.21	*Cis* methyl with 1,2 + 3,4 moieties	9300.0 ± 12.1	(38.937 ± 0.051)
Ficus elastica Roxb. Ex. Hornem (*leaf*)	Moraceae	2.0 ± 0.46	*Cis* methyl with 1,2 + 3,4 moieties	9834.0 ± 32.8	(41.173 ± 0.137)
Euphorbia antisyphylitica Zuce.	Euphorbiaceae	1.9 ± 0.40	*Cis* methyl with 1,2 + 3,4 moieties + methylene nearly *trans*	8448.0 ± 19.3	(35.370 ± 0.081)
Ficus glomerata Roxb. Cor. Pl.	Moraceae	1.7 ± 0.36	*Trans* methyl with 1,2 + 3,4 moieties + methylene nearly *trans* + vinylene protons	7670.0 ± 20.4	(32113 ± 0.085)
Carissa carandas L.	Apocynaceae	1.7 ± 0.18	*Cis* methyl with 1,2 moiety + methylene nearly *trans*	8221.1 ± 12.9	(34.420 ± 0.054)
Euphorbia heterophylla L.	Euphorbiaceae	1.7 ± 0.10	*Cis* methyl with 1,2 + 3,4 moieties + methylene nearly *trans*	7961.2 ± 25.1	(33.332 ± 0.105)
Jatropha gossypifolia L.	Euphorbiaceae	1.7 ± 0.35	Methyl 3,4 moiety	8759.0 ± 12.1	(36.672 ± 0.051)
Artocarpus hirsuta Lamk.	Moraceae	1.5 ± 0.29	Methyl 1, 2 + 3, 4 moieties	7331.0 ± 11.1	(30.693 ± 0.046)

*Values are means of three replications ± S.D.

Species containing 1.5% or more hydrocarbons are shown in Table-1. *Sarcostemma brevistigma* had the highest concentration of hydrocarbons with 3.6%. *Caralluma attenuata* had the second highest concentration of hydrocarbons with 3.4%, while *Jatropha multifida* had 3%. Seven species contained more than 2% of hydrocarbon. Thirty-three species listed below yielded 1.1–1.4% hydrocarbons. They included: *Canarium strictum* Roxb; *Plumeria rubra* L.; *Argyreia pomacea* Chois.; *Euphorbia hirta* L.; *Opuntia dillenii* Haw.; *Allamanda cathartica* L.; *Lochnera rosea* Reichb. (rose flower var.); *Pedilanthus tithymaloides* Poit.; *Antiaris toxicaria* Le'schen.; *Vallaris solanacea* O. Kze.; *Euphorbia splendens* Boj.; *Calophyllum inophyllum* L.; *Vateria indica* L.; *Gardenia gummifera* L.f.; *Aganosma cymosa* G.Don.; *Euphorbia coronaria* Stapf.; *Thevetia nerifolia* Juss (yellow flower var.); *Wrightia tinctoria* R.Br.; *Calotropis procera* R.Br.; *Marsdenia volubilis* T. Cooke; *Ficus religiosa* L.; *Clusea rosea* Jacq.; *Dalbergia sissoo* Roxb.; *Syzygium jambolanum* DC.; *Mimusops elengi* L.; *Alstonia scholaris* R.Br.; *Nerium odorum* Soland (white flower var.); *Thevetia nerifolia* Juss. (white flower var.); *Croton sparsiflorus* Morong.; *Artocarpus integrifolia* L.; *Ficus bengalensis* L.; *Ficus elastica* Roxb. Ex. Hornem and *Cymbopogon citratus* Stapf.

Gross calorific value: The gross calorific values of the screened species were comparable to well-known natural fossil fuel sources. The hydrocarbon fraction of *Fixus elastica* (leaf) had a gross calorific value of 9834 cal/g (41.17 MJ/kg), which is close to the calorific value of Mexican fuel oil (Table-2). Four species had hydrocarbon fractions containing gross calorific values of more than 9000 cal/g (37.68 MJ/kg). *Caralluma attenuata* and *Tylophora asthmatica* had moderately high hydrocarbon contents and high calorific values above 9200 cal/g (38.52 MJ/kg) (Table-1). These species could be potentially useful as an industrial raw material or as hydrocarbon feed stocks. Two species, *Plumeria rubra* and *Marsedenia volubilis,* had gross calorific values of 9426 (39.46 MJ/kg) and 9739 (40.78 MJ/kg), respectively. They are not listed in Table-1 because their hydrocarbon content was < 1.5%.

TABLE-2
ENERGY CONTENT BIOMASS AND FOSSIL FUELS OF KNOWN SOURCES*

Biomass and fossil fuels	Moisture (%)	Ash content (%)	Gross calorific values values	
			(cal/g)†	MJ/kg
Rice straw hulls	7	15	3333.0	13.955
Lignite coal	36.8	5.9	3888.0	16.278
Cattle manure	50	17	4111.0	17.212
Corn cobs	10	1.5	5167.0	21.633
Municipal refuse	43	8	5278.0	22.098
Methanol	—	—	5353.0	22.414
Anthracite coal	4.3	9.6	7111.0	29.772
Mexican fuel oil	—	—	10308.0	43.158
Crude oil			10531.0	44.091
Gasoline			11256.0	47.127

*Values are means of three replications ± S.D.
†Ref. [8] 1 cal = 4.1868.

NMR spectra: Plant species yielding 1.5% or more of hydrocarbons were subjected to NMR analysis with the result shown in Table-1. Thirteen species had hydrocarbon fractions, with seven species containing *cis*-polyisoprene compounds, while two species contained *trans*-polyisoprene compounds. *Euphorbia tirucalli* was the only species that contained both *cis* and *trans* polyisoprenes. *Jatropha multifida* and *Artocarpus hirsuta* had the 1,2 and 3,4 moieties, whereas *Jatropha gossypifolia* had only the 3,4 moiety (Table-1).

Data from Calvin's lab showed that most laticiferous plants contain 1–14% hydrocarbons[9]. Although the *cis*- and *trans*-polyisoprene components of hydrocarbons are low in concentration and molecular weight, they may be used for rubber adhesive products or as hydrocarbon feed stocks[10].

The hydrocarbon fraction of *Caralluma attenuata, Tylophora asthmatica, Cryptostegia grandiflora, Ficus elastica* (leaf), *Euphorbia antisyphylitica, Carissa carandas* and *E. heterophylla* contained the *cis*-polyisoprene compound and had a hydrocarbon yield of 1.7% or more. The *trans*-polyisoprene compound was observed in the hydrocarbon fraction of *Sarcostemma brevistigma* and *Ficus glomerata* yielding 3.6 and 1.7% hydrocarbons, respectively.

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