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Potential hydrocarbon producing species of Western Ghats, Tamil Nadu, India

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Abstract

The decline in the world supplies of hydrocarbons has lead to the search for alternate sources of fuel and chemicals. Plant species are potential sources of hydrocarbons. 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 among the plant species screened. The hydrocarbon fraction of *Ficus elastica* (leaf) had a gross heat value of 9834 cal/g (41.17 MJ/kg), which is close to the caloric value of fuel oil. Six hydrocarbon fractions contained gross heat values of more than 9000 cal/g (37.68 MJ/kg). Of the 13 species hydrocarbon fraction analysed, 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. Published by Elsevier Science Ltd.

Keywords: Cis-polyisoprene; Trans-polyisoprene; Hydrocarbon

1. 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 underutilised 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 has led us to the search for alternative sources for fuels and chemicals.

Hydrocarbons in plants, such as natural rubber (polyisoprene) have chemical structures similar to many hydrocarbons derived from petroleum (MW, 10,000), but with molecular weights (MW) 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].

Plants as a source of hydrocarbon and rubber have been investigated periodically for many years [1–5].

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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 [4]. 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.

2. Materials and methods

2.1. Collection of plant samples

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 subsampled twice. Plant samples of 46 species belonging to various families were collected from Courtallum to Srivilliputhur (RF) of 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 analysed for chemical composition. Plant materials were chopped into small pieces, allowed to dry in a sheltered area at ambient temperature ranging from 10°C to 30°C and then ground in a Wiley mill with a 1 mm sieve.

2.2. Analytical analysis

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 [2,3].

Gross heat value of hydrocarbon fraction was determined by Bomb calorimeter (Toshniwal, model cc.0.1) [6].

NMR spectrum 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 system. 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 [7,8].

2.3. Statistical analysis

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.).

3. Results

3.1. Hydrocarbon

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

Species containing 1.5% or more hydrocarbons are shown in Table 1. Three species had 3% or more of hydrocarbons. *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* Leschen.; *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.;

Table 1
Plant species from the western Ghats, India, containing 1.5% or more hydrocarbons

Name of the plant species	Family	Yield of hydrocarbon (%)[a]	Nature of hydrocarbon	Gross heat value cal/g (MJ/kg)
Sarcostemma brevistigma W. & 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)[a]
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. & 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 Zucc.	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 (32.113 ± 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)
Biomass and fossil fuels[b]				
	Moisture (%)	Ash content (%)	Gross heat values	
			(cal/g)	MJ/kg
Rice straw hulls	7	15	3333.0[b]	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

[a]Values are means of three replications, ±S.D.
[b]Ref. [9]. 1 cal = 4.1868 J.

Dalbergia sissoo Roxb.; *Syzygium jambolanum* DC.; *Mimusops elengi* L.; *Alstonia scholaris* R.Br.; *Nerium odorum* Soland (white flower var.); *Thevetia neriifolia* Juss. (white flower var.); *Croton sparsiflorus* Morong; *Artocarpus integrifolia* L.; *Ficus bengalensis* L.; *Ficus elastica* Roxb. Ex. Hornem; and *Cymbopogon citratus* Stapf.

3.2. Gross heat value

The gross heat values of the screened species were comparable to well-known natural fossil fuel sources. The hydrocarbon fraction of *Ficus elastica* (leaf) had a gross heat value of 9834 cal/g (41.17 MJ/kg), which is close to the calorific value of Mexican fuel oil (Table 1). Four species had hydrocarbon fractions containing gross heat values of more than 9000 cal/g (37.68 MJ/kg). *Carallumma attenuata*, and *Tylophora asthmatica* had moderately high hydrocarbon contents and high heat values above 9200 cal/g (38.52 MJ/kg, Table 1). These species could be potentially useful as an industrial raw material or as a hydrocarbon feed stocks. Two species, *Plumeria rubra* and *Marsedenia volubilis* had gross heat 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 $< 1.5\%$.

3.3. NMR spectroscopy

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 titucalli* was the only species that contained both cis and trans polyisoprenes. *Jatropha multifida* and *Artocarpus hirsuta* had the 1,2 and the 3,4 moieties, whereas *Jatropha gossypifolia* had only the 3,4 moiety (Table 1).

4. Discussion

Data from Calvin's lab showed that most laticiferous plants contain 1–14% hydrocarbons [10]. 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 a hydrocarbon feed stocks [11].

Natural rubber is the most common hydrocarbon polymer found in green plants. Low molecular weight natural rubber would be of interest as a plasticising additive (processing aid) to rubber mixes, for making cements (adhesives), and if economically feasible as a hydrocarbon feed stocks. Trans-polyisoprene (gutta) could have a large-scale application as both a thermoplastic and thermosetting resin if it was available at a low enough price [11].

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.

5. Conclusions

All the species screened, except for the herbs need to be established only once and would be suitable for annual pollarding. They grow profusely without any agronomic management in dry waste lands which will reduce production costs. Moreover, their ability to flourish on marginal arid and semiarid soil is an added advantage since their commercial development will not compete with other conventional agricultural crops or crop lands.

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