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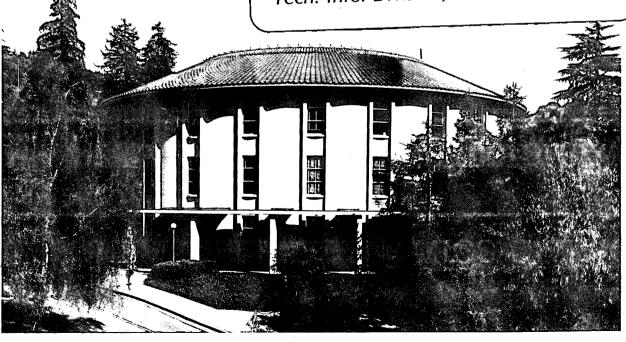
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CASSAVA -- A LATEX-BEARING PLANT FROM NIGERIA

Tunji Sonola 1 , Esther K. Nemethy 2 and Melvin Calvin 2

Abstract

Calvin (1976) and others (Nemethy, Otvos and Calvin, 1979, 1981) have investigated extensively some latex-producing plants, especially <u>Euphorbia lathyris</u>, and shown that they contain hydrocarbons which can be converted into high energy liquid fuels. A review of some latex-producing plants from Nigeria is hereby presented. Emphasis has been placed on the investigation of Cassava plant (Manihot esculenta) from the point of view of its potentialities as an economic crop, both in terms of fuel source as well as food consumption and use as a chemical feedstock (Calvin, 1977, 1979, 1980,1982).

Cassava plant (Manihot esculenta) is a genus of the Euphorbiaceae family. It was originally native to South America but has now spread slowly throughout the tropics until today it is one of the most widely cultivated of all root crops. Cassava is grown and harvested for its tuberous root crops; production figures suggest a world output of some 100 million tons per annum (Grace, 1977) and about 70% of this production

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comes from Brazil, Indonesia, <u>Nigeria</u>, Zaire and India. It is noteworthy that the bulk of the harvested material from Cassava goes for human consumption either directly or in the form of a fermented and roasted Cassava product called "Gari" (Oke, 1968).

Although there appears to be an oil glut in the world market today, there is no doubt that fossil fuel (crude petroleum) is being pumped out at a much faster rate than it is being formed beneath the earth's crust. This could well justify the prediction that the world could face an energy crisis long before food supplies become critical. Also, in a number of non-oil producing Third World countries, the demand for fossil fuels is an ever increasing burden on foreign exchange. Consequently, a number of countries have started to examine various plants as alternate sources of fuels.

The root crops of Cassava contain carbohydrates, which can be fermented into ethanol (Robinson, 1979), a product, which apart from its value as a chemical feedstock, can be used directly as liquid fuel (Paul, 1979). The production of fermentation alcohol from corn and sugar cane and subsequent use as "gasohol" (10% alcohol and 90% gasoline) has been reported (Calvin, 1980). It is now known that Brazil produces about $4 \times 10^9 \ \text{L}$ per annum of fermentation alcohol from sugar cane, and subsequent discussion about the use of "gasohol" in the United States is still in progress (Chambers, et al., 1979; Weisz and Marshall, 1979).

In this discussion we show that Cassava ($\underline{\text{Manihot}}$ esculenta) and other latex-producing plants from Nigeria contain constituents which are similar to those of $\underline{\text{E.}}$ lathyris and can therefore be converted into fuel energy. In the case of Cassava, the root crops, the stem and the leaves are all

sources of fuel energy so that its potential as an "energy farm" candidate may even be greater than those of other latex-producing crops.

AGRONOMIC YIELD

Manihot species are herbaceous perennials that thrive under the most diverse climatic conditions and at a low level of management. Traditional methods of cultivation could produce 4-12 tons/acre, while Cock (1974) reported that a preoduction figure of 40-60 tons/acre is feasible using modern agricultural practice. This would indicate a higher biomass yield than found for <u>Euphorbia lathyris</u> (see Calvin 1974,1976,1980). A typical Cassava plantation in Nigeria is shown in Fig. 1.

PLANT EXTRACTION

Solvent extraction of plant materials was carried out on the sun-dried leaves and stems (<u>Manihot esculenta</u>), whole plant (<u>Euphorbia hirta</u>) or leaves only (<u>Plumaria rubra</u>). After drying, the materials were finely ground in a Wiley mill and oven dried at 70°F to remove traces of moisture.

Various portions of materials were extracted with n-heptane and then with methanol using a Soxhlet extractor for a continuous period of eight hours for each sample. The extraction procedures were similar to those reported by Nemethy, et al. (1979, 1981).

Ten new species of latex-producing plants from Nigeria were investigated. The preliminary results are shown in Tables 1 to 5. An attempt has been made to identify the constituents of the n-heptane extract of Manihot esculenta because of its potential as an economic crop and because literature reviews to date stress the importance of the investigation of root crops (as a source of carbohydrates), seeds [as a source of fatty acids (Nartey and Moeller, 1973)], and leaves [as a source of proteins, Eggum (1970)].

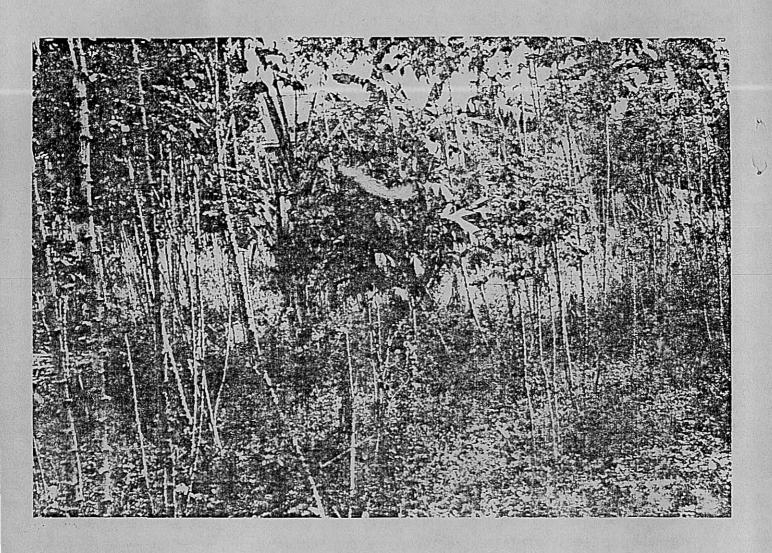


Fig. 1. Typical Cassava plantation in Nigeria

The data in Table 1 show the percentage heptane and methanol extractables of the dry weight of materials. The yields of the simple organic extractables vary from 18% to 37% of the dry weight. The C,H,O ratios and the heat of combustion values of heptane and methanol extracts are shown in Table 2. The higher oxygen contents of the methanol extracts indicate that these may well be mixtures of simple sugars in the form of hexoses as found for <u>E. lathyris</u>.

Conversion of heptane extracts to liquid fuels.

The conversion of hydrocarbon-like materials to liquid fuels has been demonstrated at the Mobil Research Corporation laboratories by W. O. Haag, et al. (1980). Similarly, terpenoid extracts from \underline{E} . lathyris have been processed under the same conditions (Calvin, et al., 1982). We have used the method suggested by Haag to compare aromatic fractions from the cracking, and the expected results from our samples are shown in Table 3. The experimental results for \underline{E} . lathyris have been taken into consideration.

Estimation of protein content of residue.

The leaves of Cassava had been reported to contain protein in up to 30% of the dry weight (Eggum, 1970). After extraction with n-heptane and methanol, we decided to determine the protein content of the residue using the percentage of nitrogen obtained in the elemental analysis. This was done for all the samples since they were obtained from plants which are all members of the Euphorbiaceae family. The results are shown in Table 4. Apart from Chrysophyllum albidum, which has a slightly higher protein content, Manihot esculenta contains 8.94% protein. This value is small compared to the value of 30% reported by Eggum (1970), but since the crude protein is said to be deficient in methionine and only marginal in tryptophan in relation to FAO reference protein, it is unlikely that the true protein content would be very much greater than 10%.

Table 1. HEPTANE AND METHANOL EXTRACTION

Sample .	Total Extractables (% dry weight)	Heptane Extract (% dry weight)	Methanol Extract (% dry weight)
		,	
<u>Manihot</u> <u>esculenta</u>	30.06	8.56	21.50
E. heterophylla	18.55	4.74	13.81
Thevetia peruviana	19.1	7.7	11.40
Plumaria rubra	24.03	5.83	18.20
E. hyssopifolia	33.88	10.68	23.20
Crysophyllum albid	<u>um</u> 38.75	8.90	29.85
E. hirta	26.17	3.75	22.42
Yellow Alamanda (<u>Alamanda carthati</u>	<u>ca</u>) 35.07	9.21	25.86
Ricinus communis	31.44	6.80	24.64
Jatropha curcas	31.61	8.20	23.41

Table 2. C,H,O RATIOS AND HEAT VALUES OF n-HEPTANE AND METHANOL EXTRACTS

Sample	n-Heptane Extract		Methanol E	xtract
·	C,H,O Ratios (formula)	Heat Values (Btu/lb)	C,H,O Ratios (formula)	Heat Values (Btu/lb)
Manihot esculenta	^{CH} 1.77 ⁰ 0.06	17.72 x 10 ³	CH _{1.82} 0 _{0.42}	9.3 x 10 ³
E. heterophylla	CH _{1.82} 0 _{0.07}	17.55 x 10 ³	CH _{2.4} 0 _{0.50}	8.15 x 10 ³
Thevetia peruviana	CH _{1.83} 00.06	17.95 x 10 ³	CH _{2.4} 0 _{0.85}	7.12 x 10 ³
Plumaria rubra	CH _{1.83} 0 _{0.06}	17.98 x 10 ³	CH _{2.45} 0 _{0.29}	12.9 x 10 ³
E. hyssopifolia	^{CH} 1.80 ⁰ 0.07	17.72 x 10 ³	CH _{2.14} 0 _{0.80}	7.09 x 10 ³
Chrysophyllum albidum	^{CH} 1.70 ⁰ 0.06	18.03×10^3	CH _{1.6} 0 _{0.50}	9.40×10^3
E. hirta	^{CH} 1.77 ⁰ 0.08	17.0 x 10 ³	^{СН} 1.99 ⁰ 0.89	7.45 x 10 ³
Yellow Alamanda (<u>Alamanda carthatica</u>)	CH _{1.77} 0 _{0.05}	18.17 x 10 ³	CH _{2.42} 0 _{0.80}	7.09 x 10 ³
Ricinus communis	^{CH} 1.77 ⁰ 0.11	16.46 x 10 ³	CH _{2.10} 0 _{0.85}	7.2 $\times 10^3$
Jatropha curcas	^{CH} 1.92 ⁰ 0.08	17.33 x 10 ³	CH _{2.42} 0 _{0.6}	8.3×10^3

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Table 3. PREDICTED CRACKING PATTERN AND PRECENT AROMATICS

OF n-HEPTANE EXTRACTS

Sample	Formula	H/C	(H/C) _{eff} .	% Aromatics
Manihot esculenta	^{CH} 1.77 ⁰ 0.06	1.77	1.65	36
E. heterophylla	^{CH} 1.82 ⁰ 0.07	1.82	1.68	35
Thevetia peruviana	^{CH} 1.83 ⁰ 0.06	1.83	1.71	34
Plumaria rubra	CH _{1.83} 0.06	1.83	1.71	34
E. hyssopifolia	CH _{1.80} 0 _{0.07}	1.80	1.66	36
Chrysophyllum albidum	CH _{1.70} 0.06	1.70	1.58	39
E. hirta	CH _{1.77} 0 _{0.08}	1.77	1.61	38
Yellow Alamanda (<u>Alamanda carthatica</u>)	CH _{1.77} 0 _{0.05}	1.77	1.67	35
Ricinus communis	^{CH} 1.77 ⁰ 0.11	1.77	1.55	41
Jatropha curcas	80.0 ⁰ 1.92	1.92	1.76	32

Table 4. ESTIMATION OF PROTEIN CONTENT OF RESIDUE

Sample	% N	% Residue	Protein Estimation as % of dry weight
Manihot esculenta	2.06	69.94	8.94
E. heterophylla	1.02	81.45	5.19
Thevetia peruviana	0.90	80.90	4.60
Plumaria rubra	0.43	75.97	2.04
E. hyssopifolia	1.66	66.12	6.86
Chrysophyllum albidum	2.63	61.25	10.07
E. hirta	1.51	73.83	6.97
Yellow Alamanda (<u>Alamanda</u> <u>carthatic</u> a)	1.46	64.93	5.92
Ricinus communis	1.76	68.56	7.50
Jatropha curcas	0.75	68.39	3.21

Chemical characterization of heptane extract of Manihot esculenta.

Thin layer chromatography (tlc) on silica gel plates using petroleum ether:ether (1:1) solvent system shows five major components. Comparison of the R_F values with authentic samples of β -amyrin $(C_{30}H_{50}0)$ and β -sitosterol $(C_{29}H_{50}0)$ indicated that two of the major components may be β -amyrin and β -sitosterol. The heptane extract was later separated by adsorption chromatography on silica gel into five crude fractions using different eluents of increasing polarity. Infrared spectra were used to determine the functional groups present in the various fractions (Table 5). Further characterization of components would necessitate the use combined of/gas-chromatography-mass spectroscopy in order to identify the major triterpenoids in the fractions. But it was obvious from infrared data that the terpenoids are present as alcohols, ketones or fatty acid esters.

CONCLUSION

The results so far obtained suggest that latex-producing plants from Nigeria, especially Manihot esculenta, may have a potential as hydrocarbon-producing crops. In order to make a full comparison of \underline{M} . esculenta with \underline{E} . lathyris, which has been extensively investigated (Calvin, et al., 1982), further chemical analyses of the constituents of \underline{M} . esculenta have to be carried out so as to establish the specific terpenoid compounds present in the extract and possibly their biosynthetic pathways. There is, however, no doubt about its value as an economic crop in terms of its use as a source of fuel energy and its nutritional significance.

Although Nigeria is an oil-producing country and a member of OPEC, the domestic consumption of refined petroleum is very much in excess of

Table 5. MANIHOT ESCULENTA--HEPTANE FRACTION
ON SILICA GEL COLUMN

Eluent	% Sample separated	C,H,O Ratios (formula)	Functional Group Present
n-Heptane	14	CH ₂	
Benzene	26	^{CH} 1.8 ⁰ 0.09	C-OR, C=C
Ethyl acetate	36	^{CH} 1.72 ⁰ 0.24	0-H, C=C, C=0
Acetone	7.0	^{CH} 1.80 ⁰ 0.26	0⊱H,C=C, C=0
Methano1	13.0	^{CH} 1.68 ⁰ 0.25	0-H,C=C, C=O

production. This makes the country an importer of refined fuel energy, thereby constituting a drain on foreign exchange. Since Cassava is very widely cultivated and the tuber products form a major staple food in several developing countries (Rogers, 1965), it may be an additional challenge for these countries to use the stems and the leaves of the Cassava as well as the tuber as sources of fuel energy and chemical feedstocks.

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