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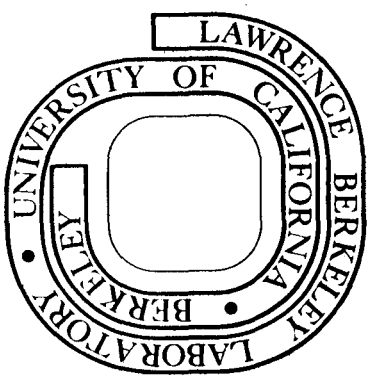

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PLANT CROPS AS A SOURCE OF FUEL AND HYDROCARBON-LIKE MATERIALS

Peter E. Nielsen, Hiroyuki Nishimura, John W. Otvos and M. Calvin

Abstract

Chemical analyses have been made of a number of plant species in order to assess their suitability as renewable sources of hydrocarbon-like photosynthetic products. Yields of rubber and wax, glycerides, isoprenoids and other terpenoids were estimated. Individual sterols were identified in some species.

It has recently been suggested[1] that certain plants rich in polyisoprenes and other hydrocarbon-like materials might be cultivated and grown as renewable sources of photosynthetic products, in addition to carbohydrates.

In order to evaluate the prospects of this idea, we have started a chemical analysis of possible plant candidates (e.g., Euphorbiaceae). Analogous work was done in 1920-30 by Hall & Long[2] and Edison[3] but in search of US-native rubber producing crops, and presently Buchanan et al. are working on overall evaluation of possible crops[4].

The analytic method of Hall & Long and Edison consisted of an exhaustive acetone extraction followed by a benzene extraction believed to contain the rubber. Although the investigators have collected a large volume of data, these are only of limited interest to us. Edison[3] did not even report the amount of acetone extractables, and Hall & Long[2] only the amount but not its chemical composition; the acetone extractables (averaging 10 percent of the total dry plant weight) generally are ten times the amount of the benzene extractables.

We have, therefore, extended the method of Hall & Long by analyzing the extracts using NMR (Table 1) and subsequently computerized gas chromatography-mass spectroscopy (GC-MS) (in progress), thereby getting both a quantitative and a qualitative analysis of the species.

As an evaluation of the plants is crucially dependent on their agricultural behavior, we have made test plantings of Euphorbia lathyris

and E. tirucalli in both Northern and Southern California, thereby hoping to obtain estimates of annual acre yields.

Furthermore, we are analyzing latex samples of these plants (Table 2)[5], the latex having a very high concentration of hydrocarbons. Though sterol analyses for most of the species here reported have been published before in connection with chemotaxonomy[6], quantitative data have not been available.

This work is only in its initial stage, and although the results obtained so far are fragmentary, we clearly see the indication that "petrochemical plantations" might be technically feasible within a few years.

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Table 1

Percent of Total Plant Dry Weight

Plant	Benzene Extract			Acetone Extract			
	Rubber	Wax	Total	Total	Glycerides	Isoprenoids	Other (Terpenoids)
Asclepias cursavica	0.6	<0.1	0.7	5.9	3.	<0.5	2.
Cryptostegia grandiflora	0.2	0.05	0.35	13.3	7.	<0.5	6.
Eucalyptus globulus	<0.01	0.05	0.1	12.	3.5	<0.5	7.
Euphorbia lathyris (leaves)	0.1	0.2	0.3	25.	13.7	2.2	8.3
E. lathyris (seeds)	-	-	-	40.	40.	<0.1	<2.
E. lathyris (stem)	-	-	-	4.5	1.9	<0.5	2.
E. marlothii	0.2	0.4	0.6	9.5	5.1	<0.5	3.3
E. tirucalli (UCB)*	0.07	0.13	0.2	5.	2.4	<0.5	2.0
E. tirucalli (UCLA)*	0.1	0.3	0.4	8.5	4.4	<0.5	3.4
Hevea brasiliensis	1.3	0.2	1.5	9.6	5.1	<0.5	2.6
Jatropha curcas	<0.1	0.6	0.7	4.2	1.5	0.8	1.4
Monadenium rhizophorum	1.2	0.2	1.4	16.5	9.	<0.5	6.
Pedilanthys sp.	<0.1	<0.1	0.5	8.7	4.7	<0.5	2.3
Sarcostemma viminale	<0.1	0.8	0.8	12.3	6.6	<0.5	4.8
Synadenium grantii	0.4	0.4	0.8	15.	6.6	<1.5	5.7

Table 1. Acetone and benzene extractables from various plants. The compound distributions are estimated on the basis of NMR-spectra (60MHz, $CDCl_3$) of the extracts (fig. 1).

* UCB = University of California, Berkeley. UCLA = University of California, Los Angeles.

Table 2

HYDROCARBONS AND STEROLS FROM LATEX

Source	% of Latex Dry Weight		Sterols Identified‡ (in Order of Abundance)
	Rubber	Sterol	
Achras sapota	14+	66	a, b
Asclepias sp. (Brazil)	3.5	31	a, b
Asclepias sp. (USA)	(12)	(72)	a, b
Euphorbia characias	-	-	g, c, j, i
E. coerulescens	1	75	d, e, m
E. lathyris	3	50	j, i, g, c, d
E. misera	-	-	d, c, i, m
E. obtusifolia	-	-	g, c, h, j, d
E. tirucalli	1	50	d, m, e
Hevea brasiliensis	87	1	k, f, l

a: α-amyrin acetate, b: β-amyrin acetate, c: cycloartenol, d: euphol, e: euphorbol, f: fucosterol, g: "iso-lanosterol", h: "iso-lanosterol", i: lanosterol, j: 24-methylene-cycloartanol, k: β-sitosterol, l: stigmasterol, m: tirucallol

Table 2 Hydrocarbon distribution in plant latices

+30% cis- and 70% trans-polyisoprene (by NMR)

other samples all cis-polyisoprene

‡Identified by gas-liquid chromatography (fig. 2) and GC/MS.

REFERENCES

1. Calvin, M. Hydrocarbons via Photosynthesis. 110th meeting of the Rubber Division, American Chemical Society, San Francisco, Oct. 1976. Calvin, M. In "Living Systems as Energy Converters", R. Buvet, et al., (eds), Elsevier/North Holland Biomedical Press, Amsterdam (1977), pp. 231-259.

2. Hall, H. M. and F. L. Long. Rubber Content of North American Plants. Carnegie Institution of Washington (1921).

3. Polhamus, L. G. (ed). Plants Collected and Tested by Thomas A. Edison as Possible Sources of Domestic Rubber. ARS-34-74, July 1967. Agricultural Research Service, USDA, Beltsville, Maryland.

4. Buchanan, R. A., I. M. Call, F. H. Otey and C. R. Russell. 110th meeting of the Rubber Division, American Chemical Society, San Francisco, Oct. 1976.

5. Nishimura, H., R. P. Philp and M. Calvin. Phytochemistry, 1977 (in press).

6. Ponsinet, G. and G. Ourisson. Adansonia, Ser. 2, 8(2), 227-239 (1968).

7. We are grateful to Professor Grady Webster, University of California, Davis, for supplying us with most of the plant samples that we have examined and Dr. R. P. Philp for his help in the interpretation of the GC/MS spectra of the sterols. The work described in this paper was sponsored, in part, by the Division of Physical Research, Energy Research and Development Administration.

FIGURE CAPTIONS

Fig. 1a NMR-spectrum of benzene extract from E. tirucalli. The resonance at 1.2 ppm is assigned to $-(CH_2)_n-$(wax) and the resonances at 1.6 and 2.0 - 2.1 ppm are assigned to methyl and methylene groups, respectively, in cis-polyisoprenes (rubber).

Fig. 1b NMR-spectrum of acetone extract from J. curcas. The resonance at 1.2 ppm is assigned to $-(CH_2)_n-$ (Glycerides) and resonances at 1.5 - 1.6 ppm and 1.9 - 2.0 ppm are assigned to methyl (cis and trans) and methylene groups in polyisoprenes.

Fig. 2. Gas liquid chromatography traces of acetylated sterols isolated from latex. The sterols were identified by coinjections with standards and by their mass spectra using GC/MS.

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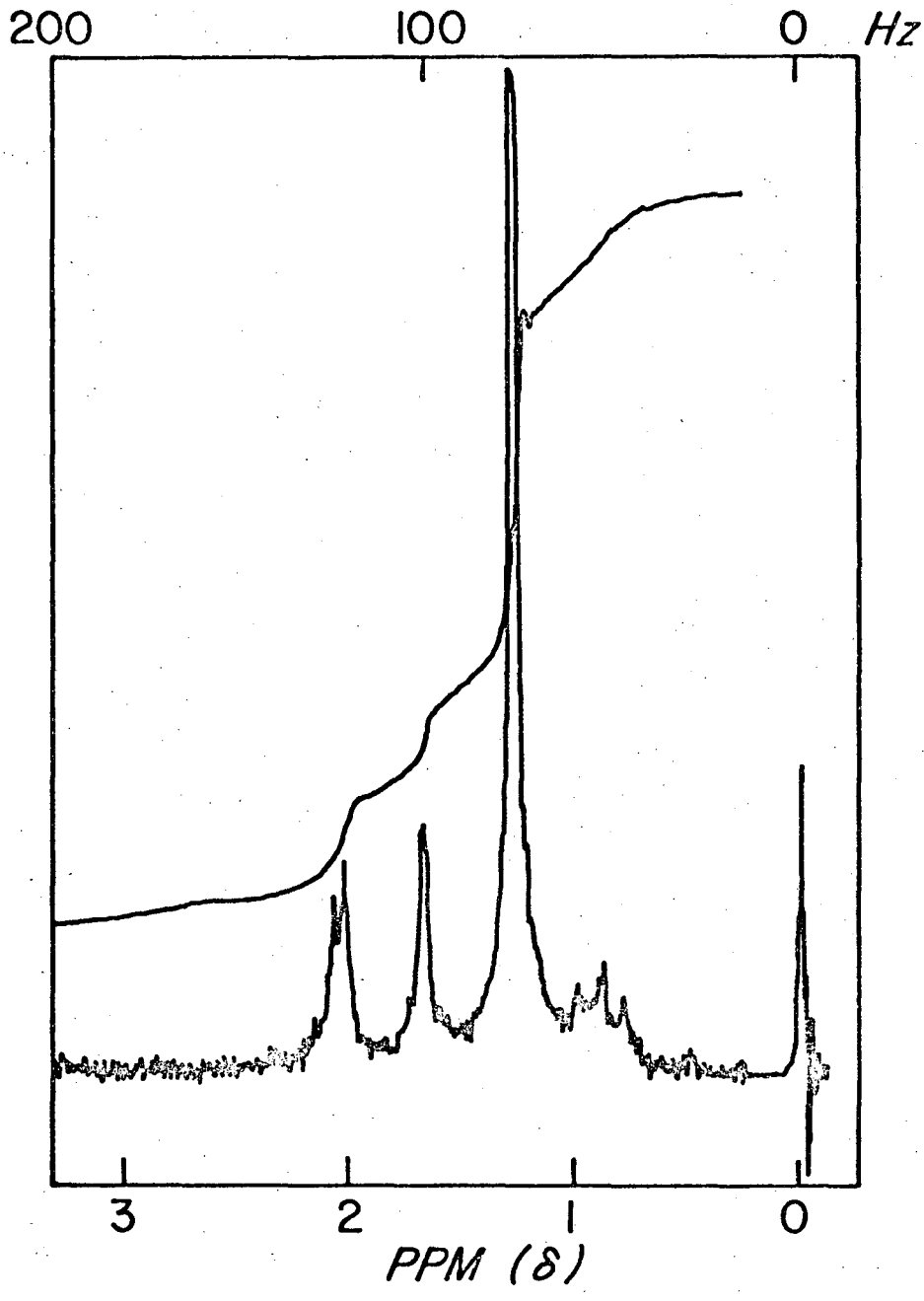

XBL 773-4313

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FIGURE 1a

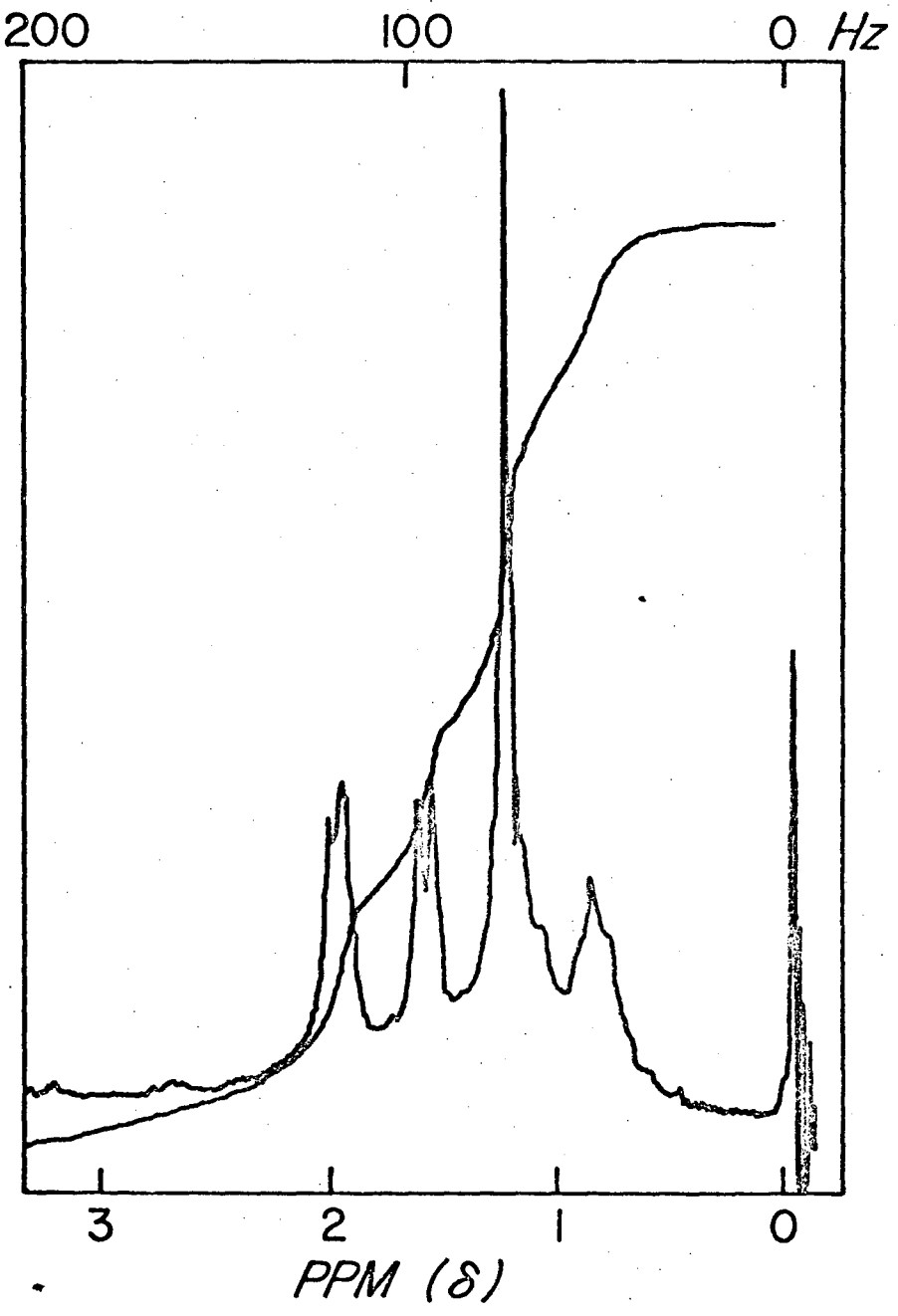

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FIGURE 1b

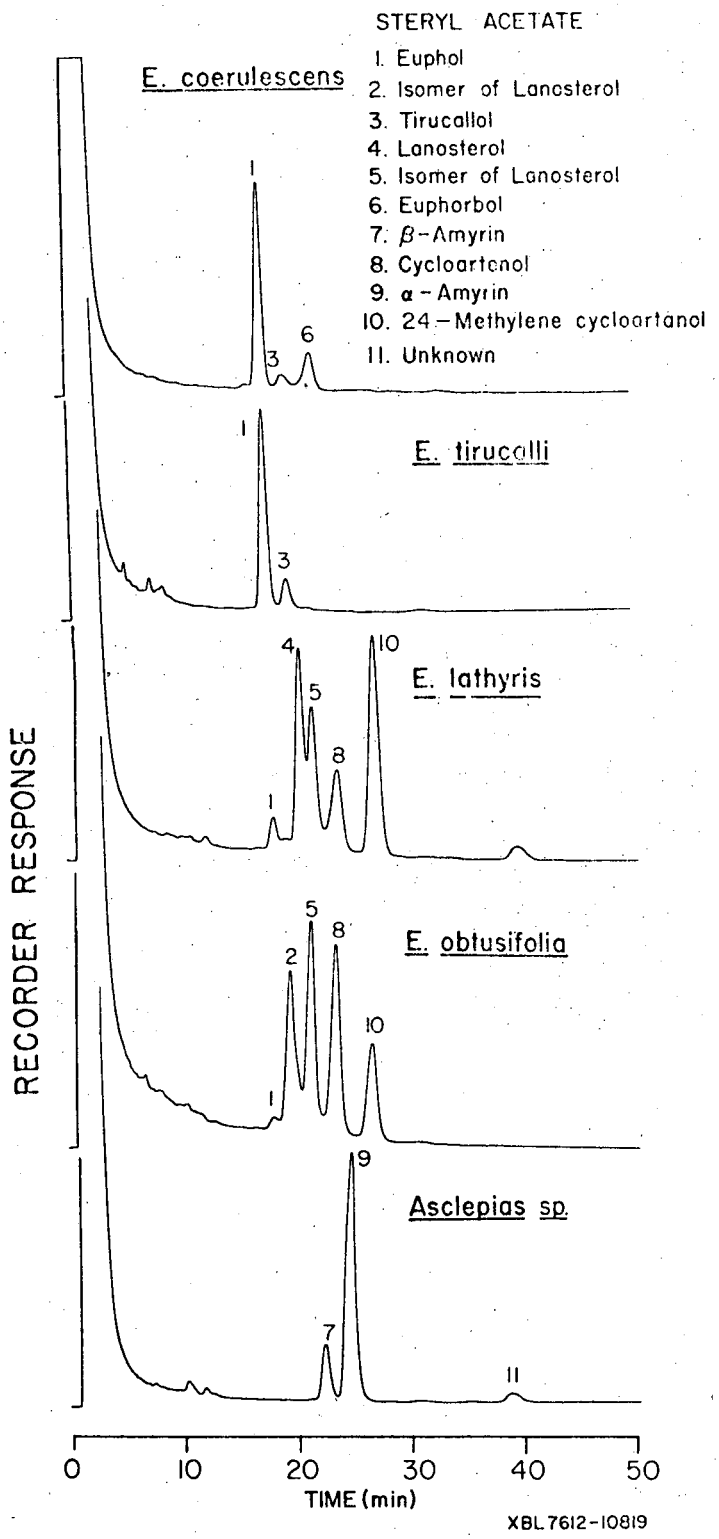

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FIGURE 2

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