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LIPIDS OF *HEVEA BRASILIENSIS* AND *EUPHORBIA COERULESCENS**

HIROYUKI NISHIMURA, R. PAUL PHILP and MELVIN CALVIN
Laboratory of Chemical Biodynamic; and the Department of Chemistry, University of California, Berkeley, CA 94720, U.S.A.†

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Key Word Index—*Hevea brasiliensis*; *Euphorbia coerulescens*; Euphorbiaceae; lipids; sterols; hydrocarbons.

Abstract—The low MW lipids identified in the latices of *Hevea brasiliensis* and *Euphorbia coerulescens* were as follows: 2-methylcyclobutanone; 2-methyl-2-hydroxycyclobutanone; 2-methylcyclobutanol; euphol; euphorbol; and tirucallol.

INTRODUCTION

As a result of decreasing supplies of fossil hydrocarbons it has become necessary to re-examine other sources of raw materials for possible conversion into hydrocarbons [1]. It is well known that sources such as sugarcane and rubber trees (*Hevea*) can produce energy-rich materials under suitable conditions [2]. Carbohydrate from sugar-cane and other plants is converted to alcohols by fermentation and subsequently to olefins by dehydration. The same olefins are currently produced by the cracking of petroleum products. On the other hand, rubber trees produce hydrocarbons directly rather than carbohydrates. There are many latex-bearing plants (some 30 000 species) whose latex does not produce rubber but are nevertheless potential sources of hydrocarbons. Although it has a similar chemical composition as petroleum, the *Hevea* hydrocarbon polymer has a somewhat different atomic arrangement and MW distribution from the hydrocarbons in petroleum [3]. If, for example, the MW distribution of the *Hevea* hydrocarbon could be reduced to less than 10 000 instead of 100 000 and 1 000 000 and the products harvested, we might have a 'fuel' tree. Furthermore, if one accepts these plants as a source of hydrocarbon rather than of elastomer (rubber), the fact that the yield of plantation *Hevea* was raised in the last thirty years from 400 lbs/acre/year to 24 000 lbs/acre/year is an indication of the potential inherent in this species through breeding.

We have examined the low MW lipid components in the latices of *Hevea brasiliensis* and *Euphorbia coerulescens* in order to find out: (a) what is in the latex; (b) what is the distribution and structure of the high MW polymers in the latices; and (c) is the ditsribution of the high MW components influenced by the types of low MW lipids present in the latex?

This article presents our initial findings from the analyses of low MW lipids in latices from *Hevea brasiliensis* and *Euphorbia coerulescens*. A report on the distribution of the high MW components will be published elsewhere [4].

RESULTS AND DISCUSSION

The lattices of the two plants were dissolved in ether or tetrahydrofuran and subsequently fractionated into neutral, basic and acidic fractions using standard separation techniques. An additional semi-polar fraction was obtained from the *Hevea* latex by sonication of the high MW precipitate (rubber) with a mixture of heptane, ethyl acetate, and methanol. The neutral and organic acid fractions were further fractionated by urea adduction. The fractions so obtained were purified by column chromatography and TLC prior to methylation and derivatization where necessary.

The quantitative distribution of the various fractions from each latex is given in Table 1. Water and high MW components, or non-THF soluble components, account for almost 95% of the material in each latex. The remaining material was composed of soluble lipids and insoluble proteins and carbohydrates.

Since our main purpose is to determine the potential usefulness of these high MW components as a sourceof hydrocarbons, information on the distribution of lower

Table 1. Comparison of yields from various fractions of the *Heavea* and *Euphorbia* latex

Species	Water soluble components	Water (%)	Organic-solvent soluble components			
			High MW (%)†	Low MW (%)†		
				Neutral	Acidic	Basic
Hevea brasiliensis	3.4	64.8	30.7	0.5	0.3	0.3
Euphorbia coerulescens	9.2	63.2	0.4	27.0	0.1	0.1

* % Total Latex. † Higher MW is material pptd. from THF by MeOH–H_2O.

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Table 2. Major components in *Hevea* lipid extract

Class of compound	Components
Hydrocarbons	$C_{18}H_{36}$, $C_{20}H_{40}$, $C_{20}H_{42}$ (branched)
Sterols	Stigmasterol, *Sitosterol,** Fucosterol (*E. coerulescens* sterols identified as euphol, euphorbol, and tirucallol)
Fatty acids	n-C_{16}, n-C_{18} and n-$C_{18:2}$
Esters	Methyl palmitate,* Methyl stearate
Fatty acids as glycerides	n-$C_{18:2}$ and n-C_{20}
Terpenes	2-Methylcyclobutanone, 2-Methylcyclobutanol* 2-Methyl-2-hydroxycyclobutanone, $C_5H_{12}O$, $C_{10}H_{20}O$
Pigments	Carotenoids

* Major components.

MW compounds and the way in which they are related to the distributions of these components will be of the utmost importance. Table 2 summarizes the major low MW components identified in each fraction by GC and computerized GC–MS. The most significant points to emerge from this data are: (1) Absence of any significant quantities of isoprenoid hydrocarbons or fatty acids. Since the high MW components are known to be polyisoprenes, significant quantities of low MW isoprenoids would have been expected to be present. (2) Major differences were observed between the sterol content of the latices. The major sterols in the *Euphorbia* latex were initially identified as being isomers of lanosterol and a homolog of an isomer or lanosterol [5–7]. Further work, including co-injection with authentic standards on GLC, has shown that these sterols are euphol, euphorbol, and tirucallol. This extends the distribution of these sterols within the Euphorbiaceae from that described by Pousinet and Ourisson [8] who reported euphol, euphorbol and tirucallol to be normally restricted to African cactus-like Euphorbiaceae. The major sterol of *Hevea* was identified as sitosterol, and no evidence was found to indicate the presence of cycloartenol as reported by Ponsinet and Ourisson [8]. (3) The most significant finding, and one which has not been reported before, was the presence of 2-methylcyclobutanone, 2-methyl-2-hydroxycyclobutanone, 2-methcyclobutanol, in the *Hevea* latex. These components were only isolated after sonication of the high MW residue. This suggests that they might have been formed by cyclisation of isoprene components, present in or formed from the rubber during this process.

EXPERIMENTAL

The sample of latex from the *Euphorbia coerulescens* was collected from botanical gardens at UCLA by tapping the plant and collecting the latex directly into tetrahydrofuran. A token specimen of this latex can be examined in the herbarium of the Univ. of Calif., Berkeley. The sample (RRIM 701) of latex from *Hevea brasiliensis* was collected by Dr. Subramaniam of the Rubber Research Institute of Malasia. The latices were extracted and separated, using standard separation techniques. Derivatization, where necessary, was performed with BF_3–MeOH (14% w/v) for methylation of organic acids and HMDS–TMCS for silylation of free hydroxyl groups. GLC analyses were performed on a Varian 2700 GC equipped with a flame ionization detector and linear temp. programmer. The analyses were performed on a micropacked capillary column, packed with 3% Dexsil 300 on 80–100 mesh Gas-Chrom Q. GC–MS analyses were carried out on a DuPont 492–1 mass spectrometer interfaced with a Varian Aerograph Model No. 204 equipped with linear temp. programmer. The column used for the GC–MS analyses was a 9 m × 0.7 mm i.d. glass capillary column packed with 1% OV-1 coated on 80–100 mesh Gas-Chrom Q. The MS data were acquired and processed using a DuPont 21-094 data system. The components were identified from GC R_t, co-injection of standards where possible, interpretation of MS and comparison of MS with that of standard compounds.

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