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HYDROCARBONS FROM EUPHORBIA LATHYRIS

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Abstract - Euphorbia lathyris, a plant which has been proposed as an "energy farm" candidate yields a total of 35% of its dry weight as simple organic extractables. Chemical analyses of the extracts show that 5% of the dry weight is a mixture of reduced terpenoids, in the form of triterpenoids, and 20% of the dry weight is simple sugars in the form of hexoses. The terpenoids can be converted to a gasoline-like substance and the sugars can be fermented to alcohol. Based on a biomass yield of ten dry tons acre^{-1} year^{-1}, the total energy that can be obtained from this plant in the form of liquid fuels is 45 X 10^{6} BTU acre^{-1} year^{-1}.

INTRODUCTION

The growing of green plants as a renewable energy source is attracting increasing interest (1). The concept of "energy farms" involves the purposeful cultivation of selected plants, either for direct use as a solid fuel, or for use as feedstock in the manufacture of more convenient liquid fuels or other energy-intensive chemicals. The latter approach, the cultivation of plants which already produce reduced organic compounds, is attractive since some hydrocarbon-like plant products may be used directly as diesel fuel. Also, the conversion of this type of plant extract to a high quality liquid fuel is expected to be energy efficient since the material is already in a reduced state.

There are many plant species which can reduce CO_2 beyond carbohydrates. One well known plant is Hevea, the rubber tree, which belongs to the family Euphorbiaeceae. This family of plants consists of approximately 2000 species, ranging from small herbs and succulents to large trees, the large majority of which produce a milky latex which is often rich in reduced isoprenoids.

Such a latex-producing plant is Euphorbia lathyris, a biennial shrub that grows wild in California. Agronomic research is under way on the cultivation of this plant; preliminary results from wild seed and without benefit of optimal fertilization and irrigation conditions indicate a dry biomass yield of 10 tons acre^{-1} year^{-1}.

Euphorbia lathyris is not amenable to tapping like some other Euphorbs. Therefore, the entire dried plant is extracted in order to obtain the reduced photosynthetic material. The plant is oven dried at 70°, for 48 hours to 4% moisture content, then ground in a Wiley mill to a 2 mm particle size. This material is then extracted with a boiling organic solvent for 8 hours in a Soxhlet apparatus. We have found that an 8 hour time period is sufficient; longer extractions do not increase the yield.

Different solvents can be used to extract various plant constituents. One scheme which yields cleanly separated fractions and reproducible results is shown in Fig. 1.

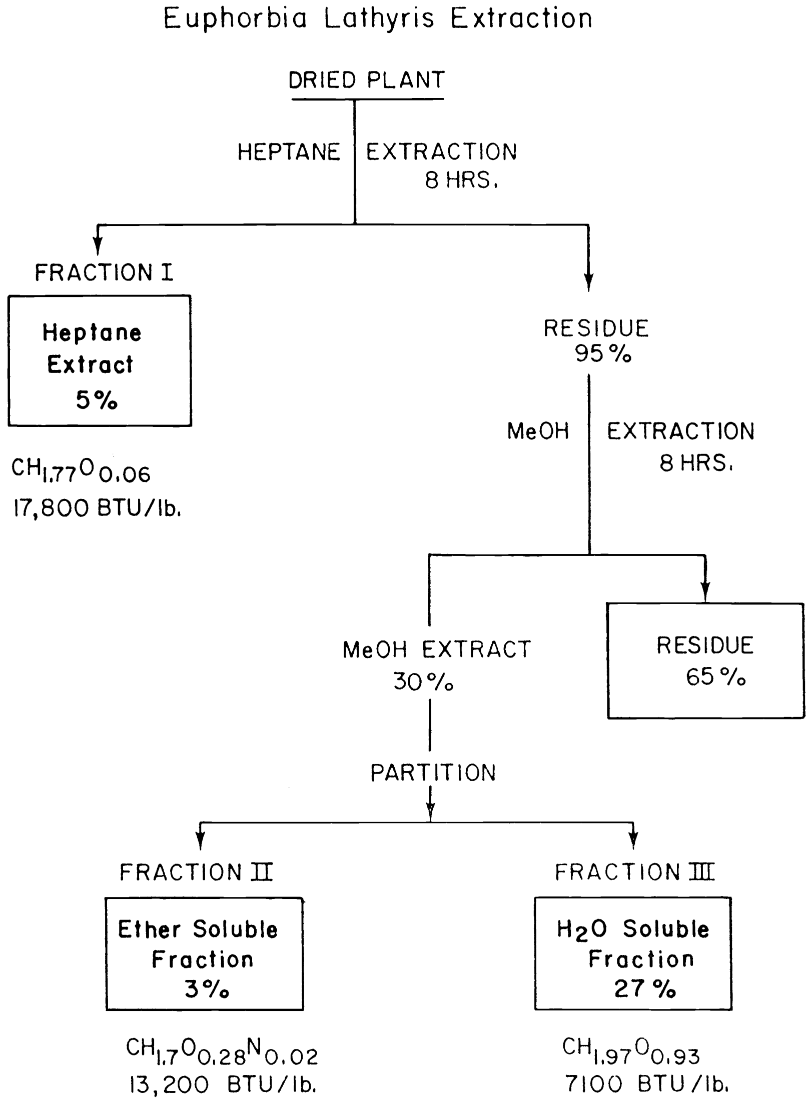

Fig. 1. Euphorbia lathyris extraction.

Acetone can also be used as the initial solvent instead of heptane; however, acetone brings down a variable amount of carbohydrates which precipitate out of the solution. These can be filtered off, leaving behind a pure acetone soluble portion, which is 8% of the dry weight of the plant. This is equivalent to the sum of Fractions I and II of the extraction scheme shown in Fig. 1.

The two fractions we have analyzed in detail are the heptane extract (Fraction I) and the water soluble portion of the methanol extract (Fraction III). The low oxygen content and high heat value of the heptane extract indicates a potential for use as fuel or chemical feedstock material; because the amount of methanol extract is substantial we investigated its chemical composition as well.

THE TERPENOIDS (HEPTANE EXTRACT)

The heptane extract is a very dark green material which contains approximately 6% chlorophyll. This complex mixture can be separated further by adsorption chromatography by eluting with solvents of increasing polarity. The characteristics of the resulting fractions are shown in Table I.

Table 1. Silica Gel column on heptane fraction

SILICA GEL COLUMN ON HEPTANE FRACTION

Eluent		Elemental	(Class of Compounds)
I, heptane	7%	CH_2	Hydrocarbon
II, benzene	33%	$CH_{1.72}O_{0.03}$	Fatty Acid Esters of Triterpenoids.
III, EtoAc	41%	$CH_{1.67}O_{0.07}$	Tetra and Pentacyclic Triterpenoids. Ketones. Alcohols.
IV, Acetone	5%	$CH_{1.63}O_{0.15}$	Phytosterols and Bifunctional Compounds.
V, MeOH	15%	$CH_{1.69}O_{0.22}$	Bifunctional Triterpenoids.

We have examined each of the column fractions further by gas chromatography and have obtained structural information on the major components by combined gas-chromatography-mass spectroscopy (GC/MS). Molecular formulae were obtained by high resolution mass spectroscopy (2).

The data from the GC/MS analyses show that over one hundred individual compounds comprise the heptane extract. About 50 of these are major ones; these we have either identified or classified. The major part of the heptane extract consists of various tetra- and pentacyclic triterpenoids functionalized as alcohols, ketones or fatty acid esters. Two representative structures are shown in Figure 2.

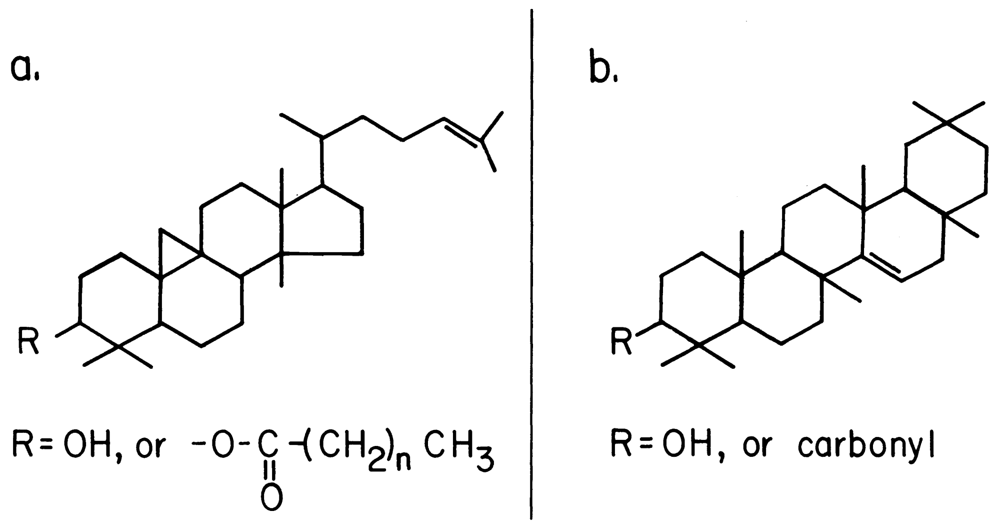

Fig. 2. Representative structures for tetra- and pentacyclic triterpenoids found in Euphorbia lathyris. The carbon skeletons shown are those of cycloartenol (a), and taraxerol (b).

Triterpenoids arise via the enzyme mediated cyclization of squalene 1,2-oxide followed by rearrangement sequences to yield a large array of interrelated C_{30} compounds. In Euphorbia lathyris, terpenoid biosynthesis is evidently shunted almost exclusively via this pathway; no major amounts of any other class of terpenoids have been detected. Several derivatives of the macrocyclic diterpenol lathyrol and of the tetracyclic diterpenol ingenol have been identified as very minor components (∿0.1%) of Euphorbia lathyris latex and seed oil (3). Some of the ingenol esters exhibit irritant and tumor promoting activity one tenth that of phorbol-13-acetate-12-tetradecanoate, the most active and well know tumor promoter. The major components of the latex, however, are five triterpenoids; they comprise 50% of its dry weight (4). The whole plant extract is also composed mostly of triterpenoids, but in a much greater structural variety, indicating that terpenoid synthesis does occur in other parts of the plant.

The only non-triterpenoid components of the heptane extract are two long chain hydrocarbons, which comprise column fraction I and a small quantity of fatty alcohols isolated from column fraction III. The two hydrocarbons are straight chain waxes: n-$C_{31}H_{64}$ and n-$C_{33}H_{68}$; the three fatty alcohols are $C_{27}H_{53}OH$ $C_{28}H_{57}OH$ and $C_{29}H_{57}OH$. These compounds, however, represent only ∿8% of the total heptane extract, so 85% of this extract is composed of only one class of natural products: triterpenoids.

If this Euphorbia lathyris terpenoid extract is to be used as conventional fuel, then further processing of this material is necessary. The conversion of biomass derived hydrocarbon-like materials to high grade transportation fuels has recently been demonstrated by Mobil Research Company (5). Various biomaterials such as triglycerides, polyisoprenes and waxes can be upgraded to gasoline-mixtures on Mobil's shape selective Zeolite catalyst. The terpenoid extract of Euphorbia lathyris was processed under similar conditions with this catalyst (6). The product mixture and distribution are shown in Fig. 3.

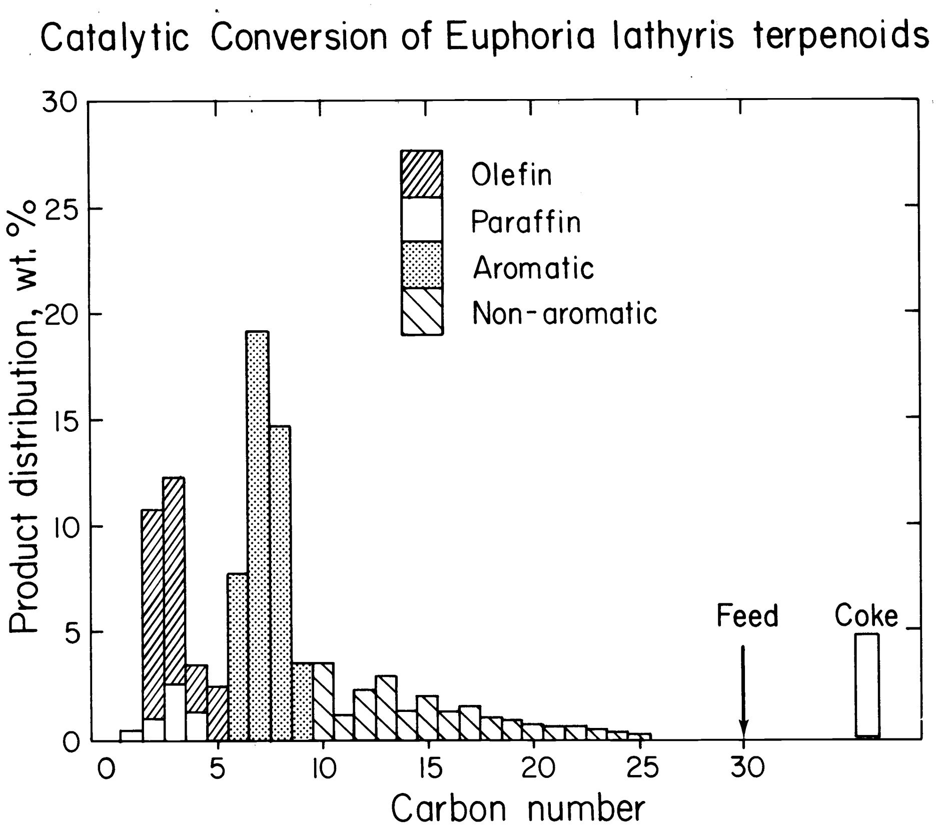

Fig. 3. Catalytic conversion of Euphorbia lathyris terpenoids.

The products obtained from the conversion of Euphorbia lathyris terpenoids seem to simulate a gasoline-type mixture; furthermore, they are rich in compounds which are premium raw materials for the chemical industry.

THE CARBOHYDRATES (METHANOL EXTRACT)

As the data in Fig. 1 indicate, a substantial amount (30%) of the dried plant weight can be extracted with methanol. The empirical formula of the water soluble portion of this extract is indicative of carbohydrates.

Since simple hexoses can be directly fermented to ethanol, a useful liquid fuel, we have determined the carbohydrate content of Euphorbia lathyris and identified the specific sugars.

The results of gel-permeation chromatography of Fraction III (Biogel-P-2) indicated that there are no poly- or even oligosaccharides present in this fraction. The carbohydrate containing fractions were identified by the Molish test, and were further characterized by two-dimensional paper chromatography and high pressure liquid chromatography (HPLC). In both of these systems only four simple sugars were detected: sucrose, glucose, galactose and fructose. The HPLC trace of the total sugar fraction as well as the relative amounts of the individual components are shown in Fig. 4.

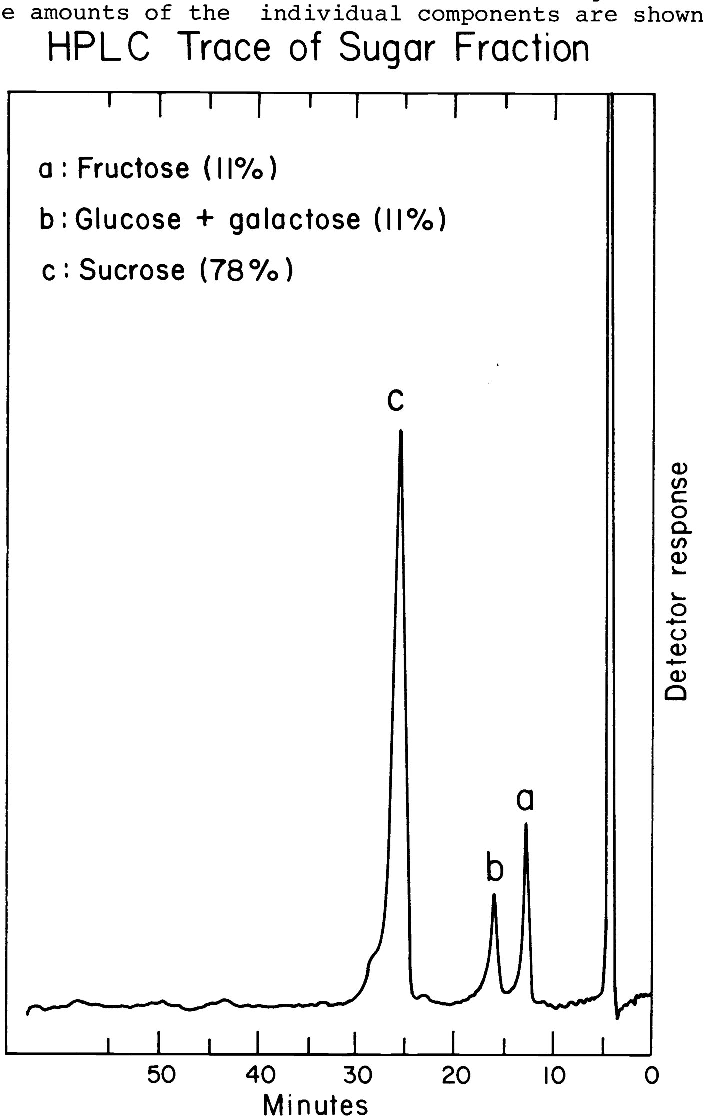

Fig. 4. HPLC trace of sugar fraction. Altex NH_2 column. Mobile phase: $CH_3CN:H_2O$, 80:20. R.I. x 8. a:fructose, b:glucose + galactose, c:sucrose. Ratio a:b:c = 1:1:7.4

These four simple sugars represent 20% of the dry plant weight, or two-thirds of the water soluble portion of the methanol extract.

We have obtained some preliminary information on the nature of the non-carbohydrate components of this sample. The material balance and the identity of some other compounds are shown in Fig. 5.

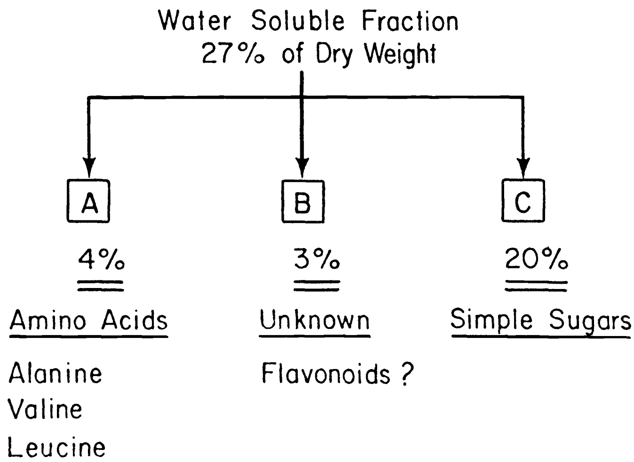

Fig. 5. Components of the water soluble fraction. (Fraction III of Fig. 1).

The amino acids listed in Fig. 5 were identified by paper chromatography; the tentative assignment of flavonoid structure to fraction B is based on their characteristic absorption spectra.

We have determined that the entire crude carbohydrate (Fraction III, Figure 1) extract is fermentable to ethanol without further purification. Since there is certainly no specific yeast available for Euphorbia sugar fermentation, we have tried several different types: Brewers yeast, Bakers yeast and two yeasts used in the wine industry: Champagne and Montrachet. The best results were obtained with the Montrachet type, a yeast which is very tolerant to phenolic impurities. The fermentations were carried out on 200 ml of an approximately 10% sugar solution to which 130 mg of commercial wine yeast nutrients were added. The temperature was maintained at 23°C for 90 hrs. Under these conditions an 80% fermentation efficiency was obtained, yielding 8.4 ml of ethanol from 25 gm of the crude water extract. This alcohol yield corresponds to 66% fermentable sugar content of the sample based on the established fermentation efficiency, and is in excellent agreement with the chromatographic data shown in Figures 4 and 5.

DISCUSSION

We can therefore obtain not only hydrocarbons from Euphorbia lathyris but a substantial quantity of ethanol as well. Our present biomass yield of 10 dry tons acre^{-1} yr^{-1} yields 5.3 bbls of crude extract which is converted to gasoline, and 2 tons of sugars, fermentable to alcohol.

A conceptual process study for the large scale isolation of these useful chemicals has recently been developed by SRI International (7). This process is based on solvent extraction, an existing technology in the seed oil industry. The overall scheme and the energy balance are shown in Fig. 6.

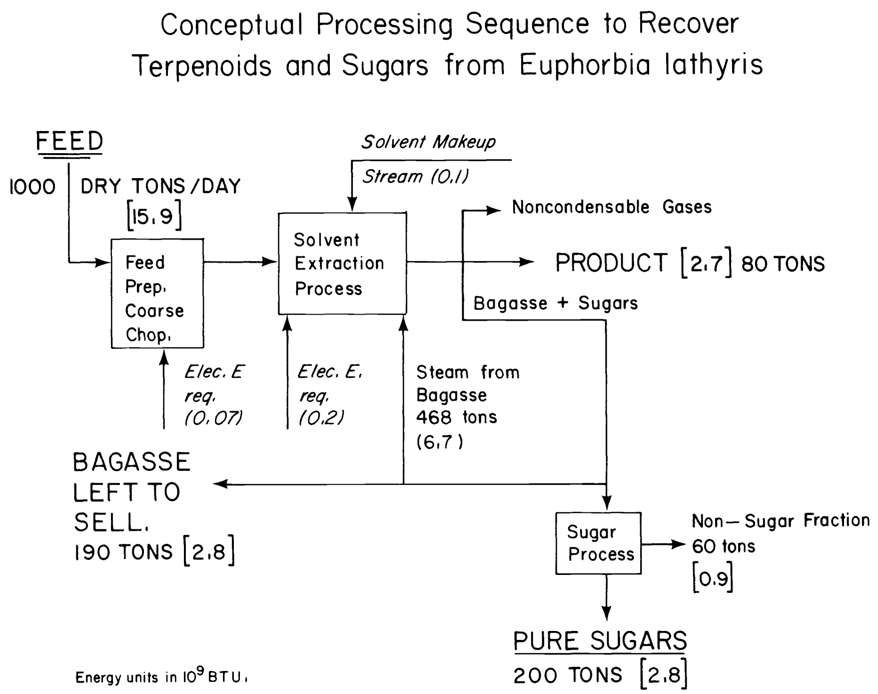

Fig. 6. Conceptual processing sequence to recover terpenoids and sugars from Euphorbia lathyris

As seen in Figure 6, the cellulosic plant residue (bagasse) is used to generate the energy required for solvent extraction and recovery. According to this model, a considerable quantity of bagasse is left over after recovery of the useful products. If an estimate of the required energy input for cultivation of the plants is included in this model, the entire process still remains energy positive (8).

Euphorbia lathyris and other potential hydrocarbon-producing crops are new species from the point of view of cultivation. With further agronomic research and plant selection the biomass as well as the terpenoid yield is expected to increase. Nevertheless, it is interesting to compare in terms of energy yield a new crop like Euphorbia lathyris to other established crops such as corn or sugarcane. The liquid fuel yield from corn is 16×10^6 BTU $acre^{-1}$ $year^{-1}$; from sugarcane it is 45×10^6 BTU $acre^{-1}$ $year^{-1}$, both in the form of ethanol. The potential Euphorbia lathyris yield is 25×10^6 BTU $acre^{-1}$ $year^{-1}$ in the form of hydrocarbons and 20×10^6 BTU $acre^{-1}$ $year^{-1}$ in the form of alcohol, for a total yield of 45×10^6 BTU $acre^{-1}$ $year^{-1}$.

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