LBL-16872
Preprint c.2

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

CHEMICAL BIODYNAMICS DIVISION

Submitted to CRC Critical Reviews in Plant Biology

BIOMASS AS A SOURCE OF LIQUID FUEL

RECEIVED
LAWRENCE
BERKELEY LABORATORY

DEC 13 1983

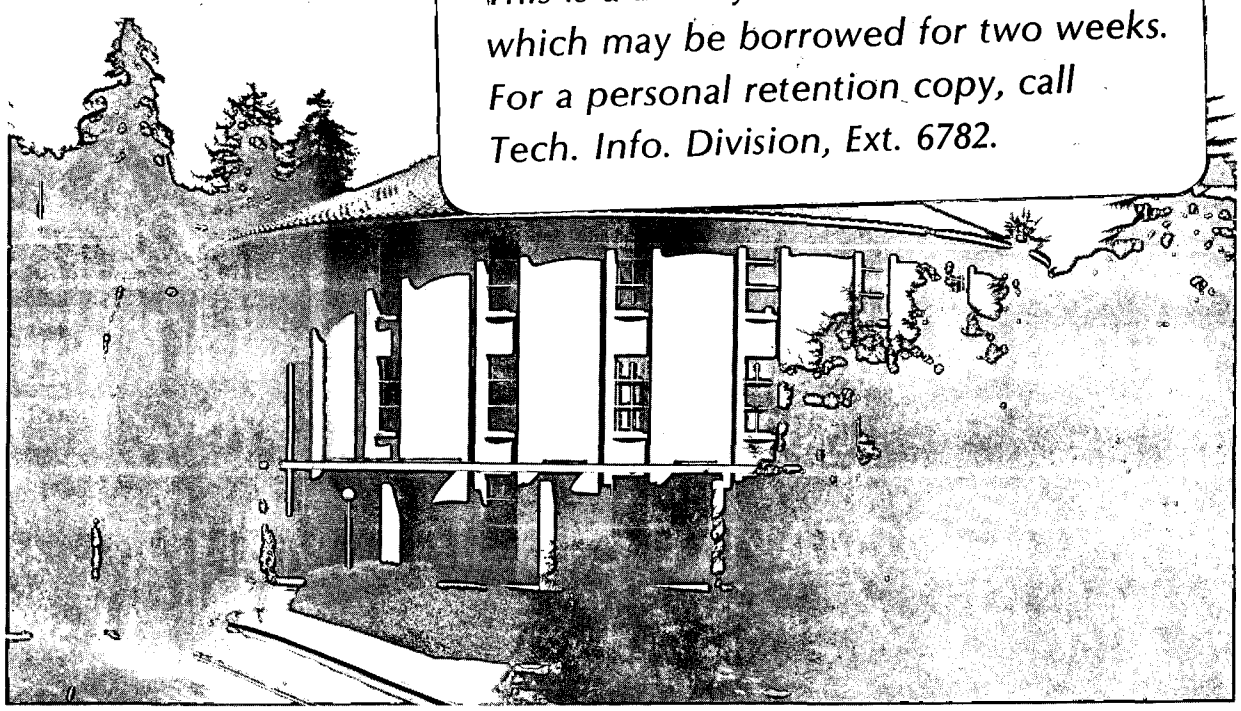
LIBRARY AND
DOCUMENTS SECTION

E.K. Nemethy

October 1983

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-16872 c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

BIOMASS AS A SOURCE OF LIQUID FUEL

E. K. Nemethy

Lawrence Berkeley Laboratory

University of California

Berkeley, California 94720

The use of green plants for the production of renewable resources, specifically for high-energy liquid fuels and valuable chemicals is discussed. The predominant classes of natural products that plants produce as pure hydrocarbons, or with a sufficiently low degree of oxygenation so that they can be catalytically reformed to pure hydrocarbons, are represented by glyceride oils and by various isoprenoids. A number of different plant species have been proposed and are being investigated as candidates for energy crops. The results of several surveys of hydrocarbon producing plants conducted over the last five years are discussed, as well as some new potential sources of hydrocarbons, with emphasis on the quantity and quality of the chemicals obtainable from these plants.

Introduction

During the last decade considerable interest has developed in the use of biomass as a renewable resource to help meet our future energy needs. Numerous proposals for the utilization of different biomass components for energy and materials have been presented in recent years and the concept of "energy farms" has been much discussed.[1-19]

The utilization of biomass as wood as well as the attendant research and technologies of lignocellulose conversion and lignin degradation have been extensively discussed in the literature and several recent reviews are already in existence.[20-25] The use of established seed oil crops as a source of diesel oil, as well as the development of new seed oil crops for industrial oils has also been the subject of recent reviews.[26-32] The subject of this review will therefore be limited to research on plants that naturally produce organic materials in a highly reduced state, and thus the whole plant extract can be used as chemical feedstock material for the production of pure hydrocarbons.

Selection of Hydrocarbon Producing Plants

Early efforts in the search of candidate species for hydrocarbon production were concentrated on polyisoprene or rubber-producing species, the great majority of which are latex-bearing plants. Buchanan and coworkers surveyed 100 plants from Illinois for natural rubber as well as "oil" content, and developed a selection criteria for the best candidates.[33] Each species was rated independently in four categories: fiber utility, protein production, oil and rubber production. Oil and rubber contents were determined by extraction of dried plant material with various solvents. The extraction scheme involved using acetone as the first solvent followed by benzene. The acetone extract was partitioned between hexane and ethanol; the hexane soluble portion was termed "oil" and the ethanol solubles as the "polyphenol" fraction. The term

polyphenol fraction seems to have been employed as an operational definition for the alcohol solubles; later work has shown substantial carbohydrate content in these extracts.[34] In this survey 14 species were identified, which were judged to have good potential as hydrocarbon and rubber producing crops according to the criteria of Buchanan and coworkers. The most promising candidates were among three plant families, Euphorbiaceae, Asclepiadeceae and Compositae.

A more recent survey of eighty species from the southeastern U.S. and southern Great Plains was reported by Adams and McChesney.[35] The effectiveness of different solvent systems, acetone/cyclohexane, cyclohexane/ethanol and cyclohexane/methanol were tested. Continuous extractions in a soxhlet apparatus for 20 hrs were found to be superior to other methods such as shaking and decanting. Significant differences were found between the extraction efficiencies of methanol and ethanol; methanol was found to be superior for the removal of polar material in every case. The most striking case was Helianthus annuus; methanol extraction yielded 250% more material from this plant than ethanol. Considerable variation was found in the quantity of total extractables among the 80 species, from a low of 8.3% to a high of 53%. Five of the 80 species gave total extractable yields in excess of 30%: Baccharis neglecta (Asteraceae) 32.5%, Ilex glaba (Aquitoliaceae) 32.2%, Juniperus monosperma leaves (Cupressaceae) 38.5%, Sapium sebiferum leaves (Euphorbiaceae) 32.7% and Rhus glabra (Anacardiaceae) 53%. Only four species gave cyclohexane extractables in excess of 10%: Grindelia squarosa (Asteraceae) 12%, Juniperus monosperma 14%, Mammillaria heydei (Cactaceae) 13% and Sapium sebiferum 10%.

McLaughlin and Hoffman conducted an extensive survey of over 400 collections of plants from southwestern U. S.[36] The plant collections encompassed considerable taxonomic diversity; 195 species in 107 genera in 35 families were examined for hydrocarbon or chemical feedstock production. A two

step solvent extraction using cyclohexane followed by ethanol was used in this survey. The term "biocrude" was coined by McLaughlin et al. to describe the extractable material. Initially, biocrude was defined as the total extractables, i.e. the sum of the cyclohexane plus ethanol extracts, later however biocrude was redefined as only the cyclohexane portion of the total extract.[37] One of the results of this survey is depicted in Fig. 1. A correlation between a high percentage cyclohexane extractables and resinous or latex-bearing plants was found. Another major finding was the inverse proportionality of high biocrude content and plant size. Smaller, potentially lower total biomass producers yielded higher % of biocrude, thus the authors concluded that for arid regions high biomass yields are not necessary for the economic production of biocrude. Ten species were identified by the Arizona selection criteria as having high potential for further develoment: Pedilanthus macrocarpus (Euphorbiaceae), A. albicans, A. subulata and A. erosa (Asclepiadaceae), Amsonia grandiflora, A. kearneyama and A. grandiflora (Apocyanaceae), Crysothamnus paniculatus, C. nauseous, Grindelia camporum and Xanthocephalum gymnospermoides (Compositae).

Two species in the family Asclepiadaceae: Calotropis procera and Asclepias syriaca have been investigated as potential sources of hydrocarbon-like materials. Erdman et al.[38] extracted dried Calotropis procera with hexane followed by methanol. Six month old plants as well as different plant segments, stems, leaves and pods were examined for % hexane and % methanol extractables. Hexane extractions yielded 4.4, 3.8, 5.1 and 9.4% (w/w); methanol extractions gave 16.1, 18.5, 12.1 and 21% (w/w) from whole plants, stems, leaves and pods respectively. The heats of combustion for the various extracts (calculated from

the elemental compositions) were reported: all the hexane extracts had heats of combustion comparable to that of crude oil (10,000 cal/g) the methanol extracts were considerably lower (4500 cal/g).

These results are comparable to that of Peoples and Lee, who examined C. procera cultivated in Arizona[39]. C. procera is also being considered for energy use in Australia; preliminary results by Williams et al.[41-43] on the Australian plants are essentially the same as those reported by Peoples and Erdman.

T. A. Campbell reported on the properties of Asclepias syriaca, the common milkweed.[44] This study was designed to assess the chemical and agronomic variation present in this species in Maryland and northern Virginia. In a two year replicated evaluation of progenies from 41 populations significant agronomic differences (15% level) were found. Buchanan's extraction technique (acetone followed by hexane) was used as the chemical assay; extractions with methanol were not done in this case. The acetone extract was defined as the polyphenol plus oil fraction and the hexane extract as the polymeric hydrocarbon fraction. A range of 4.7-14.4% in the acetone extracts and 0.2-1.2% in the hexane extract was found. These fractions were not partitioned any further, nor characterized in any other manner.

Adams also reported on the yield of A. syriaca but in this case the hexane-methanol extraction scheme was used.[45] The yield of hexane extractables was 3-4%, and the yield of methanol extractables was 19%. The calculated heats of combustion were 9500 cal/g and 4160 cal/g respectively.

These exploratory screenings are essential in the evaluation of potential oil yields from new sources. Although no single extraction procedure may be found which is optimal for every one of the great number of species that should be screened, a standardization of the extraction techniques is necessary for the purpose of valid comparisons. For the case of E. lathyris for example it was

found that acetone does extract various amounts of carbohydrates, and thus the % acetone extract cannot be replicated with any degree of accuracy.[46] The use of nonpolar solvents, such as cyclohexane, heptane or hexane do give more reproducible results. These extracts labeled variously "oil" "biocrude" "hydrocarbon" or "polyphenol" need to be further characterized and defined. For the purpose of initial screening studies the determination of elemental compositions and/or heats of combustion does serve this purpose.

Chemical Composition of Biocrude

Among the large number of species screened for oil production only a few have been subjected to further analyses in terms of the specific chemical composition of the nonpolar and polar extracts. Detailed structural information has been reported to date on the composition of four candidate species: *A. speciosa*, *E. lathyris*, and *Grindelia camporum* and *Chrysonthanus paniculatus*. Buchanan and coworkers have fractionated the nonpolar extractables of *A. syriaca* and *E. lathyris* into general lipid classes and obtained semi-quantitative data based on TLC scanning and densitometry.[51] The complete analysis of the nopolar extract of *A. speciosa* has recently been reported by Adams et al.[47] The two triterpene acetates α and β-amyrinacetate comprised 62% of the sample in a ratio of 5:1 respectively. Several other esters of amyrin, butyrate, caproate and palmitate comprised another 15% of the mixture. Low molecular weight cis-polyisoprene (Mw=52,000) was also found in the crude hexane extract but only in ca. 2% concentration. Only trace amounts (0.5%) of fatty alcohols, alkanes, phytosterols, mono- di- or triglycerides were found. The main constitutents of the methanol extract of *A. speciosa* were also identified as myo-inositol and sucrose.[52]

The composition of *Euphorbia lathyris* extracts was much more complex than that of *A. speciosa*.[48] Approximately 50 compounds, almost all tetra- and

pentacyclic triterpenoids functionalized as ketones, alcohols and fatty acid esters constitute the heptane extractables of this plant. Representative structures are shown in Fig. 2. The composition of E. lathyris latex has also been investigated, five tetracyclic triterpenols and fatty acid esters of these are stored in latex.[53] All of the latex components could also be detected in the whole plant extract, however the latter yields a much greater variety of triterpenoids than the latex. The large structural diversity of the whole plant triterpene fraction indicates that triterpenoids are stored and probably synthesized in other parts of the plant not just the latex. It is estimated that a maximum of 15-20% of the whole plant hexane extract is latex-derived.

Euphorbia lathyris also stores a substantial amount of simple sugars, fermentable to ethanol. Analysis of the methanol extract (30% of plant dry wt) showed the presence of four simple sugars, sucrose, glucose, galactose and fructose. These four sugars represent 20% of the plant dry weight.[54,55]

The chemistry of Grindelia camporum and Chrysothamnus paniculatus, resinous plants under development as arid land crops in Arizona have been investigated by Timmerman et al.[49,50]. Grindelia resin yield range has been reported to be 5-15% of the dry weight; the amount of acid fraction of the crude resin is highly variable and may constitute 20-90% of the resin. The acid fraction consists primarily of grindelic acid and its derivatives. A series of these grindelane diterpenoids have been isolated and identified; the structures of these resin acids are shown in Fig. 3. Grindelic acid itself has been found to be the major constituent constituting from 40 to 80% of the resin acid fraction of G. camporum. These resin acids may be converted to lower molecular weight hydrocarbons, or they may serve as substitutes for resin products in the naval stores industry.

Oddities

A great number of species so far have been proposed as candidates for high grade fuel or chemical feedstock production. Many have been included in screening projects, evaluated and discussed as viable sources of hydrocarbons. In this section three sources of hydrocarbons that have not been included in any of the previously cited surveys will be discussed. Each of these has some unique characteristics, and each has received some attention as a source of liquid fuels. Copaifera langsdorfii, a tropical tree, has been suggested as a source of diesel fuel; Pittosporum resiniferum bears fruits that have been referred to as the "petroleum nut"; the fresh water alga Botryococcus braunii is a unique organism in its ability to synthesize and secrete substantial quantities of hydrocarbons.

Copaifera

Species of the genus Copaifera (Leguminosae) are important forestry trees in South and Central America, and may be cultivated in the U.S. in areas such as Puerto Rico or Florida. The trees synthesize resin and all organs and secrete this material into intercellular species. In the trunk of the mature tree cavities formed by the breakdown of resin secretory cells coalesce into large resin containing pockets. This resin can be released by a natural or man-made opening in the bark, thus these trees can actually be tapped for oil. It was estimated that the mature tree could produce 40-60 liters of oil annually.[13,56]

The chemical composition of the resin depends on the species, and qualitative differences within a species have also been observed.[57] In some species diterpenoid acids predominate, but as much as 50-90% of the oil of C. langsdorfii is sesquiterpene hydrocarbons. A commerical resin sample of Copaifera consisted of 24 sesquiterpene hydrocarbons, 19 of which have been identified.[58,59] The diterpene acids, which constitute the rest of the resin have been identified as kaur-16-en-19-oic acid, 16-β-kaur-en-19-oic acid and

polyalthic acid.[60] These diterpene acid constitutents are detrimental from the point of view of diesel fuel use, and would have to be either modified or eliminated. Copaiba oil can also be processed by the Mobil zeolite catalyst to yield high grade gasloine.[61]

Pittosporum

Pittosporum resiniferum (Pittosporaceae) a 30m tree native to the Phillipines bears walnut size fruit rich in light oil. Even the unripe green fruit burns brilliantly when ignited, and some mountain people us the nuts for fuel. It is also used as a torch light, pressed into bamboo tubes.[62] Early reports attributed the volatility and flammability of the nut to high concentrations of n-heptane in the oil. Recent analysis of the oil showed small percentages of n-heptane and n-nonane; the major constituents were found to be two monoterpene hydrocarbons α-pinene (38%) and myrcene (40%).[63] Hexane or methylene chloride extraction yields 8-10% of the fresh fruit weight as a fragrant orange oil.

P. resiniferum has two fruiting seasons per year; the size of the fruits as well as the total yield is variable. Preliminary data indicate a yield 6-10 kg of fruits per year for the smaller size ones and 12-18 kg per year for the larger ones. The cultural management of this plant is still in the early stages; plantations of P. resiniferum are being planned in the Phillipines. Projected planting densities are 2x2 meters or 2x3 meters, which, based on the present range in oil and fruit yield, would result in a total oil yield of 6.6 to 10 bbl per acre/year.[64]

Botryococcus braunii

The colonial green alga Botryococcus braunii is widely distributed in termperate and tropical regions where it occurs primarily in fresh waters. Colonies are often observed floating on the surface of undisturbed waters; this

buoyancy is attributed to the large amounts of accumulated oil in the alga. In the so called resting state Botryococcus has been reported to produce as much as 86% of dry weight as oil,[65] although a more typical range of oil concentration is 25-40%.[66]

The hexane extracted Botryococcus oil is orange, due to the presence of carotenoids. After removal of the pigments a clear oil is obtained which contains a homologous series of unusual isoprenoids. This series emcompasses linear isoprenoids from C_{30} to C_{37}, M W 410 to 508.[67] The structure of the C_{34} compound named Botryoccoccene has been elucidated.[68] More recently the structure of the C_{36} compound christened Darwinene has been reported.[69] (Fig. 4). Preliminary spectroscopic data on the other homologues indicate the same backbone structure with a different number of exomethylene functionalities attached to the backbone.[70] Thus the C_{30} compound appears to be an isomer of squalene, with the peculiar ethylidene group at the same position in the molecule as in botryoccoccene.[71] Botryoccoccene braunii has been reported to be a very slow growing organism; however, under favorable conditions a dry wt. doubling time or 40 hrs can be achieved in the resting state.[72] This alga also has the ability of diverting an unusually large proportion of metabolic carbon into hydrocarbon biosynthesis. Uptake studies with $H_2{}^{14}CO_3$ showed that in 1 hr 60% of the total incorporated radioactivity was associated with the hexane soluble components; 50% of the radioactivity in the hexane soluble fraction was associated with the isoprenoid hydrocarbons.[72]

Botryococcus has several attributes that suggest its potential as a renewable source of hydrocarbons, although several questions, particularly about culturing conditions, need to be answered before this organism can be critically evaluated as a fuel producer. It is, however, unique among alga in its ability to synthesize and accumulate high levels of hydrocarbons. These hydrocarbons are

are suitable as feedstock material or as transport fuels. Hydrocracking of Botryococcus derived oil yielded 62% petroleum, 15% aviation fuel, 15% diesel fuel and 3% heavy oil.[73]

Catalytic Reforming of Biocrude

While some low molecular weight plant hydrocarbons can be used directly as transportation fuel, and even seed oils, which are mostly triglycerides, have been tested as diesel substitute, the very viscous, often solid whole plant extracts of resinous and latex bearing plants need to be upgraded for liquid fuel use. Mobil Research Co. has demonstrated that the use of the size and shape selective zeolite catalyst of the ZSM-5 type that is used in the methanol to gasoline process, can be extended to produce gasoline and aromatics from plant extracts. The process has been demonstrated for diverse classes of plant products. Glyceride oils, such as corn and castor oil, as well as the long chain linear esters of jojoba oil can be efficiently converted to high quality chemical components or fuel (gasoline).[74]

The tri- and diterpenoid constitutents of plants such as Euphorbia, Asclepias and Grindelia can also be upgraded by a somewhat modified fluid bed process to similar products.[61] The product distribution obtained from E. lathyris extract is shown in Fig. 5.

The product distribution, specifically the yield of the petrochemically important BTX (Benzene, toluene, xylene) aromatics, was found to be a strong function of the effective hydrogen to carbon ratio of the feed. Thus most reduced photosynthetic products, even polyisoprenes, can be converted to high grade fuel and petrochemicals by this process.[61]

Economic Potentials

The topic of energy and economic analyses of biomass projects has been the subject of much debate.[75-81] Considerations of economic feasibility, however,

are critical elements in the development of energy crops for liquid fuel production.

Predictions for the final cost of one bbl of biocrude range over an order of magnitude from $20 to $200.[9,37,82,83] Although conceptual analyses are potentially useful for future research, they often suffer from uncertainties and ambiguities in the input data.

Buchanan et al. examined the economics of multi-use botanochemical crops.[84] These preliminary cost-assessments for crop production, collection and processing predicted that new and radically different multi-use agricultural systems would be economically attractive. Projected specifications, i.e. the requirements that would have to be met for successful development of new botanochemical crops were developed. For a herbaceous, perennial, whole-plant oil producing crop these specifications were: biomass yield (total dry matter): 16,000 lb/acre, whole plant oil plus polyphenol fraction: 3360 lb total or 21% of the dry biomass, crude protein 1401 lb, leaf meal (720% protein), 5120 lb, fiber: 960 lb.

Conceptual studies of hydrocarbon recovery for E. lathyris have been developed by SRI International, Chevron and most recently by the Office of Arid Land Studies in Arizona. The most complete SRI scenario predicted $100 per bbl of Euphorbia crude,[83] which is in good agreement with the more current estimate by the Office of Arid Land Studies,[37] even though E. lathyris was found to be unsuitable for cultivation in arid lands.[85]

For arid land crops McLaughlin et al. estimated that the resinous plants Gridelia comporum and Chrysontamus paniculates would be able to produce one bbl of biocrude at a cost of approx. 50-60/bbl.[37]. At these predicted costs

biocrude would still not be competitive at this time with imported petroleum. However, the use of these plant products as substitute petrochemicals may be economically favorable.

Prognosis and Conclusions

Biomass development for the production of liquid fuels and high value chemicals is still in its formative stages. However, the results that emerged from the research programs conducted over the past five years do delineate the basic problems as well as the important areas for future research. In this field it is generally recognized that biomass research must be an integrated endeavor with agronomic, engineering, chemical, biochemical and environmental research components. However, one important limitation to the development of bioenergy crops for liquid fuel use is the apparent upper limit of approximately 15% per dry weight of reduced photosynthetic material that plants surveyed to date seem to produce. An increase in this percentage, even without a corresponding increase in total biomass yield, is predicted to have a positive effect on the final cost of a barrel, whether this barrel is used for chemicals or for fuel.[83]

There are only a few reported cases of secondary metabolite yield enhancement in higher plants. Improvement in monoterpene yield by application of paraquat,[86] in Hevea rubber yield by classical breeding methods[87] and in guayule rubber yield by bioinduction have been reported.[88,89] The method of bioinducers under investigation today in guayule may find applications in eliciting higher yields of various low molecular weight terpenes, although preliminary experiments with E. lathyris did not increase triterpenoid content.[90] It is encouraging, however, that the mechanism of action of these compounds is beginning to be investigated. Recently, Benedict et al. reported on the effect of one bioregulator, 2-(3,4-dichlorophenoxy)-triethylamine on

rubber yield and on enzyme activities in guayule.[91] The activities of several enzymes on the isprenoid pathway were tested; increases in mevalonate kinase, IPP isomerase, rubber transferase and FPP synthetase activities were observed.

One major obstacle to rapid improvement of hydrocarbon yields is our limited knowledge of the fundamental biochemical mechanism, including regulation, of secondary plant products. Progress is being made, most notably in the area monoterpene biochemistry.[92] However, the biochemistry of the largest terpenoid class, sesquiterpenes, remains essentially unexplored. For example, it is not known today whether sesquiterpene hydrocarbons are metabolic end products, or whether they are re-utilized, or turned-over by plants. Such information would be important in assessing maximum hydrocarbon productivity.

Conventional plant breeding which has been of great importance for the production of better and more useful plants will undoubtedly be also important in the development of energy crops. Its main limitations are the length of time required to produce new varieties, and often the relatively small gene pool available for crossings. The new biotechnologies that are just beginning to be exploited in the plant sciences, may in the future have applications in plant hydrocarbon production.

However, basic research in biochemistry and in molecular genetics are an essential prelude to genetic engineering efforts in energy agriculture.

Acknowledgment: The preparation of this paper was sponsored by the Assistant Secretary for Conservation and Renewable Energy, Office of Renewable Energy, Biomass Energy Technologies Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

1. Szego, G. C. and Kemp, C. C. Energy forests and fuel plantations, Chemtech, 3, 275, 1973.

2. Johnson, T. D. and Hinman, C. W. Oils and rubber from arid land plants, Science, 208, 460, 1980.

3. Bagby, M. O., Buchanan, R. A., and Otey, F. H., Multi-use crops and botanochemical production, in Biomass as a Nonfossil Fuel Source, Klass, D. L. Ed., A. C. S. Washington, D. C., 1980, Chap. 6.

4. Hall, D. O., Renewable resources (hydrocarbons), Outlook Agric.,10, 246, 1980.

5. Coffey, S. G. and Halloran, G. M., Higher plants as possible sources of petroleum substitutes, Search 10, 423, 1979.

6. Lipinsky, E. S. Kresovich, S. J. and Scantland, A., Fuels from new crops, in Renewable Resources: a Systematic Approach, Campos-Lopez, E., Ed., Academic press, New York, 1980, 307.

7. Lipinsky, E. S., Chemicals from biomass: petrochemical substitution options, Science, 212, 1465, 1981.

8. Calvin, M., Petroleum plantations for fuel and materials, Bioscience 29, 533, 1979.

9. Calvin, M., Green factories, Chem. & Eng. News. 50(12), 30, 1978.

10. Calvin, M., Petroleum plantations. in Solar Energy: Chemical Conversion and Storage, Hautalona, R. R., King, A. B. and Kutal, C. Ed. The Humana Press, Clifton, New Jersey, 1, 1979.

11. Calvin, M.., Fuel from plants. Sciquest, 52(7), 16, 1979.

12. Calvin, M., Nemethy, E. K., Redenbaugh, K. and Otvos, J. W., Plants as a direct source of fuel, Experientia, 38, 18, 1982.

13. Calvin, M. J., New sources for fuel and materials, Science, 219, 24, 1983.

14. Wang, S. and Huffman, J. B., Botanochemicals: supplements to petrochemicals, Econ. Bot., 35, 369, 1981.

15. Tideman, J. and Hawker, J. S., The hydrocarbon content of some latex bearing plants in Australia, Search, 12(10) 364, 1981.

16. Khoshoo, T. N., Energy from plants: problems and prospects, Proc. 69th Ind. Sc. Cong. Part II, 1, 1982.

17. Döbereiner, J, Neto, J. S. A., Arkcoll, D. B., Energy alternatives from agriculture, in: Pontificiae Academiae Scientiarum Scripta Varia, 46, 430, 1981.

18. Vergara, W. and Pimentel, D., Fuels from biomass: comparative studies of the potential in five countries USA, Brazil, India, Sudan and Sweden, Adv. Energy Syst. Technol. 1, 125 (1978).

19. Schooley, F. A., Dickerson, R. L., Kohan, S. M., Jones, J. L., Meacher, P. C., Ernest, K. P., Crooks, G., Miller, K. A., and Fong, W. S., A study of biomass derived fuels and chemicals likely to achieve U. S. market penetration in the years 1985, 2000 and 2020. ACS/CJS Joint Chemical Congr., Honolulu, Hawaii.

20. Bungay, H. R., Overview of new biomass industries: priorities in biotechnology research for international development, Proc. Workshop, Washington, D.C., Natl. Acad. Press, 1982.

21. Goldstein, I. S. ed. Organic Chemicals from Biomass, CRC Press Inc. Boca Raton, Fla, 1981.

22. Miller, I. J. and Fellows, S. K., Liquefaction of biomass as a source of fuels or chemicals, Nature, 289, 398, 1981.

23. Brown, R. D. and Jurasek, L., Hydrolysis of cellulose: mechanisms of enzymatic and acid catalysis. Advances in Chemistry, Series 181, Amer. Chem. Soc. Washington, D.C., 1979.

24. Crawford, D. L., Bioconversion of plant residues into chemicals: production of chemicals from lignin, Biosources Dig. 2, 52, 1980.

25. Goldstein, I. S., Perspectives on production of phenols and phenolic acids from lignin and bark, Appl. Polymer Symp. No. 28, 259, 1975.

26. Goodier, B. I. G., Heilman, M. D., Nixon, P. R., and Schwiesow, W. F., Sunflower oil--an emergency farm fuel?, Agric. Eng. 61, 20, 1980.

27. Princen, L. H., New crop development for industrial oils, J. A. O. C. S., 56, 845, 1979.

28. Beard, B. H., The sunflower crop, Sci. Amer. 244(5), 150, 1981.

29. Pryde, E. H., Nonfood uses of commercial vegetable oil crops, in Crop Resources, Siegler, D. S. Ed., Academic Press, N. Y. 24, 1977.

30. Buchanan, R. A. and Otey, F. H. Multi-use oil- and hydrogen-producing crops in adaptive systems for food, material and energy production, Biosources Dig. 1, 176, 1979.

31. Venturia, L., Alternativas de energia para os motores diesel, Energia, 2, 45, 1980.

32. Onion, G. and Bodo, L. B., Oxygenate fuels for diesel engines: a survey of world-wide activities, Biomass, 3, 77, 1983.

33. Buchanan, R. A., Cull, I. M., Otey, F. H., and Russell, C. R., Hydrocarbon and rubber producing crops, evaluation of U. S. plant species, Econ. Bot. 32, 131, 1978.

34. Calvin, M., Nemethy, E. K. Redenbaugh, K., and Otvos, J. W. Plants can be a direct source of fuel, Petroculture, 2, 26, 1981.

35. Adams, R. P. and McChesney, J. D., Phytochemicals for liquid fuels and petrochemical substitutions: extraction procedures and screening results, Econ. Bot. 37, 207, 1983.

36. McLaughlin, S. P., and Hoffman, J. J., Survey of biocrude-producing plants from the southwest, Econ. Bot. 36, 323, 1982.

37. McLaughlin, S. P., Kingsolver, b. E., and Hoffman, J. J., Biocrude production in arid lands, Econ. Bot. 37, 150, 1983.

38. Erdman, M. D. and Erdman, B. A., Calotropis procera as a source of plant hydrocarbons, Econ. Bot., 35, 467, 1981.

39. Peoples, T. R., and Lee, C. W., Dry matter and hydrocarbon yields of calotropis procera, Biomass, 2, 153, 1982.

40. Tideman, J. and Hawker, J. S. The hydrocarbon content of some latex-bearing plants, in Australia, Search, 12, 364, 1981.

41. Williams, L. R. and Home, V. N. Ether extraction of latex producing plants, Search, 14, 48, 1983.

42. Williams, L. R., Plant Crops for fuel and Energy, National Conference on Fuels from Crops, Melbourne, Australia, Sept. 1981.

43. Williams, L. R., Casali, J. and Home, V. N., Evaluation of some Australian plant species for potential as hydrocarbon producing crops, Chemistry in Australia, Sept. 1981.

44. Campbell, T. A., Chemical and agronomic evaluation of common milkweed, Asclepias syriaca, Econ. Bot. 37, 174, 1983.

45. Adams, R. P., Production of liquid fuels and chemical feedstocks from milkweed, in: Inst. Gas. Tech. Proc. Energy from Biomass and Wastes VI., Klass, A. L. Ed., 113, 1982.

46. Nemethy, E. K., unpublished results.

47. Adams, R. P., Balandrin, M. F., Hogge, L., Craig, W., and Price, S., Analysis of the nonpolar extractables of Asclepias speciosa, J.A.O.C.S., 60, 1315, 1983.

48. Nemethy, E. K., Otvos, J. W. and Calvin, M., Analysis of Extractables from one Euphorbia, J.A.O.C.S., 55, 647, 1978.

49. Timmermann, B. N., Luzbetak, D. J., Hoffman, J. J., Shivanana, D. J., Schram, K. H., Bates, R. B., and Klenck, R. E., Grindelane diterpenoids from Grindelia camporum and Chrysothamnus paniculatus, Phytochem, 22, 523, 1983.

50. Hoffman, J. J., and McLaughlin, S. P., Constituents of Chrysothamnus paniculatus (Compositae): Chrysothame, a new diterpene, and 6-oxogrindelic acid, J. Org. Chem., 47, 1725, 1982.

51. Buchanan, R. A., Otey, F. H., Russell, C. R., and Cull, I. M., Whole plant oils, potential new industrial raw materials, J.A.O.C.S. 55, 657, 1978.

52. Adams, R. P., Balandrin, M. F. and Martineau, J. R., The showy milkweed Asclepias speciosa: a potential new semi-arid land crop for energy and chemicals, Biomass, in press.

53. Nielsen, P. E., Nishimura, H., Liang, Y. and Calvin, M., Steroids from euphorbia and other latex-bearing plants. Phytochem., 18, 103, 1979.

54. Nemethy, E. K.., Otvos, J. W., and Calvin, M., Hydrocarbons from Euphorbia lathyris, Pure and Appl. Chem. 53, 1101, 1981

55. Nemethy, E. K., Otvos, J. w., and Calvin, M., Natural production of high-energy liquid fuels from plants, in Fuels from Biomass and Wastes, Klass, D. L., and Emert, G. H., Eds., Ann Arbor Sci., Ann Arbor, Mich. 405, 1981.

56. Alencar, J. da Cruz, Estudos silvicuturais de uma populacao natural de Copaifera multijuga Leguminosaw, na Amazonia central 2. producao de oleo resena, Acta Amazonia 12, 75, 1982.

57. Langenheim, J. H., Terpenoids in the Leguminosae, Adv. in Legume Systematics, Polhill, R. M., and Raven, P. H. Ed. 627, 1981.

58. Wenninger, J. A., Yates, R. L. and Dolinsky, M. J. Assoc. Off. Analyt. Chem., 50, 1304, 1967.

59. Arrhenius, S. P., Foster, C. E., Edmonds, C. G., and Langeheim, J. H. Sesquiterpenes in leaf pocket resins of Copaifera species, Phytochem. 22, 471, 1983.

60. Ferrari, M., Pagnoni, U. M.., Pelizooni, F., Lukes, V., and Ferrari, G., Terpenoids from Copaifera langsdorfii, Phytochem., 10, 905, 1971.

61. Haag, W. O., Rodewald, P. G. and Weisz, P. B., Catalytic production of Aromatics and Olefins from Plant Materials, presented at 2nd Chemical Congress of Amer. Chemical Society, Las Vegas Nev. 1980.

62. Noble, B., More secrets of the petroleum nut, Canopy 4, 4, 1978.

63. Nemethy, E. K. and Calvin, M., Terpenes from Pittosporaceae, Phytochem, 21, 2981, 1982.

64. Fernandez, E. C. personal communication, 1982.

65. Brown, A. C., Knights, B. A., and Conway, E., Hydrocarbon content and its relationship to physiological state in the green alga Botryococcus braunii, Phytochem., 8, 543, 1969.

66. Wake, L. V. and Hillen, L. W., Nature and hydrocarbon content of blooms of the alga Botryococcus braunii occurring in Australian freshwater lakes. Aust. J. Mar. Freshwater Res. 32, 353, 1981

67. Wolf, F. R., Botryococcus braunii: An unusual hydrocarbon-producing alga, Appl. Biochem. and Biotechnology, in press.

68. Cox, R. E., Burlingame, A. L., Wilson, D. M., Eglington, G. and Maxwell, J. R., Botryococcene - a tetramethylated acyclic triterpenoid of algal origin. J.C.S. Chem. Comm. 284, 1973.

69. Galbraith, M. N., Hillen, L. W., and Wake, V. Darwinene: A branched hydrocarbon from a green form of Botryococcus braunii, Phytochem. 22, 1441, 1983.

70. Wolf, F. R., The ultrastructure and hydrocarbons of Botryococcus braunii Kützing (Chorophyceae), Ph.D. thesis, Texas A & M University, 1981.

71. Hawkins, D., Nemethy, E. K., and Calvin, M., unpublished results.

72. Wolf, F. R., personal communication, 1983.

73. Hillen, L. W., Pollard, G., Wake, L. V., and White, N., Hydrocracking of the oils of Botryococcus braunii to transport fuels, Biotechnology and Bioengineering, Vol. XXIV, 193, 1982.

74. Weisz, P. B., Haag, W. O., and Rodewald, P. G., Catalytic production of high grade fuel (gasoline) from biomass compounds by shape selective catalysis, Science, 206, 58, 1979.

75. Weisz, P. B. and Marshall, J. F. High-grade fuels from biomass farming: Potentials and constraints, Science, 206, 24, 1979.

76. Kyle, B. G., High-grade fuels and biomass farming, Science, 210, 807, 1980.

77. Weisz, P. B. and Marshall, J. F. Fuels from biomass, a critical analysis of technology and economics. Marcel Dekker, Inc., New York, 1980.

78. Coffey, S. G. and Halloran, G. M., Euphorbia - perspectives and problems. presented at National Conference on Fuels from Crops, Melbourne, Australia, Sept. 1981.

79. Sachs, R. M., Low, C. B., McDonald, J. B., Awad, A. R., and Sully, M. J. Euphorbia lathyris: A potential source of petroleum-like products. Cal. Agric., July-August 29, 1981.

80. Harris, G. S. and Green, S. J., The individuality of projects for production of energy from biomass, Biomass, 3, 235, 1983.

81. Palsson, B. O., Fathi-Afshar, S., Rudd, D. F., Lightfoot, E. N., Biomass as a source of chemical feedstocks: An economic evaluation, Science, 213, 513, 1981.

82. Kohan, S. M., Extraction of hydrocarbon liquids from Euphorbia type plants, in: Mission Analysis for the Federal Fuels from Biomass Program. Vol. VI. Mission Addendum. Report No: SAN-0115-T4, 51, 1979.

83. Wilhelm, D., Recovery of hydrocarbon-like compounds and sugars from Euphorbia lathyris, SRI International report, 1980.

84. Buchanan, R. A., Otey, F. H., and Hamerstrand, G. E., Multi-use botanochemical crops, an economic analysis and feasibility study. Ind. Eng. Chem. Prod. Res. Dev., 19, 489, 1980.

85. Kingsolver, B. E., Euphorbia lathyris reconsidered: Its potential as an energy crop for arid lands, Biomass, 2, 281, 1982.

86. Roberts, D. R. Inducing lightwood in pine trees by paraquat treatment. USDA Forest Serv. Res. note SE-191, 4, 1973.

87. Archer, B. L., Polyisoprene, in Secondary Plant Products, Encyc. of Plant Physiol. New Series. Bell, E. A., and Charlwood, B. V., Eds. 8, 309, 1980.

88. Yokoyama, H., Hayman, E. P., Hsu, W. J., and Poling, S. M., Chemical bioinduction of rubber in guayule plant, Science, 197, 1076, 1977.

89. Hayman, E. P., Yokoyama, H., and Gold, S., The effect of bioregulators on the accumulation of rubber in guayule, J. Ag. Food Chem., in press.

90. Nemethy, E. K., unpublished results.

91. Benedict, C. R., Reibach, P. H., Madhavan, S., Stipanovic, R. V., Keithly, J. H., and Yokoyama, H., Effect of 2-(3,4-dichlorophenoxy)-triethylamine on the synthesis of cis-polyisoprene in guayule plants (Parthenium argentatum), Plant Physiol., 72, 897, 1983.

92. Loomis, W. D. and Croteau, R., Biochemistry of terpenoids, in the Biochemistry of Plants, Vol. 4. Lipids: Structure and Function, Stumpf, P. K., and Conn, E. E., Eds., Academic press, New York, 364, 1980.

Figure Captions

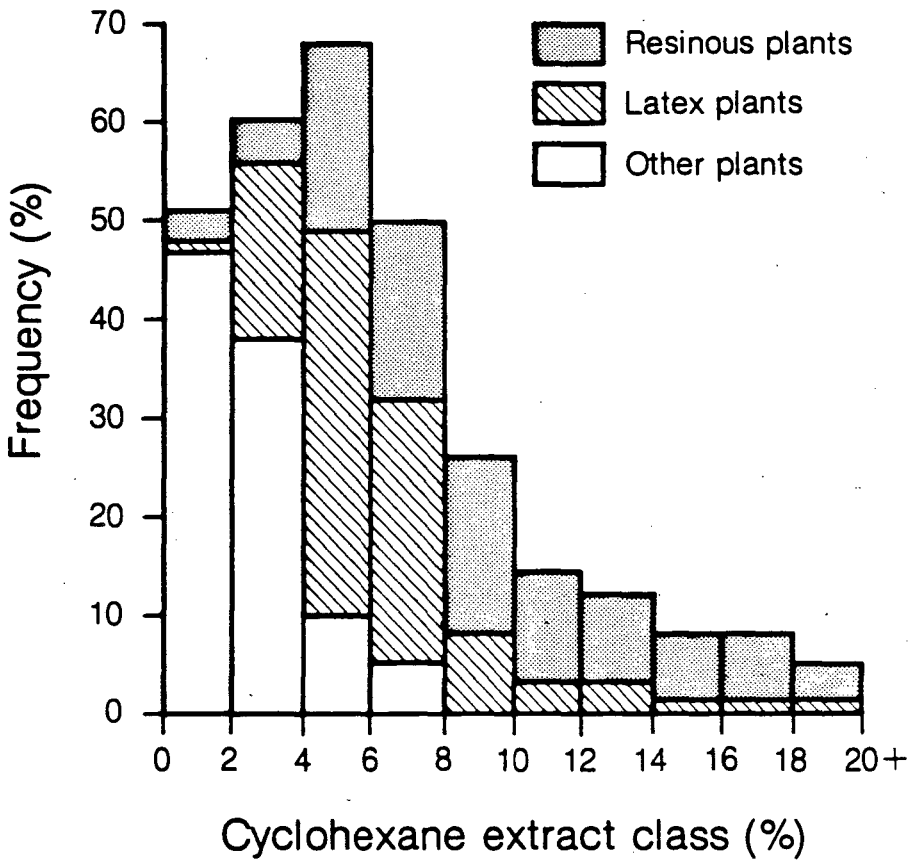
Fig. 1. Frequency distributions of percentage cyclohexane extract resinous, latex and other plants. (From McLaughlin and Hoffman, 1982).

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

Fig. 3. Structures of Grindelane diterpenoids isolated from *G. camporum*. (from Timmerman et al. 1983).

Fig. 4. Structures of Botryococcene and Darwinene (from Cox et al. 1973 and Galbraith et al. 1983).

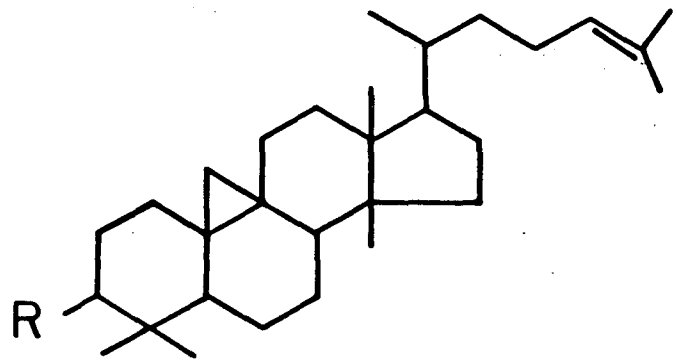
Fig. 5. Catalytic conversion of *E. lathyris* terpenoids (from Haag et al. 1980).



XBL8310-601

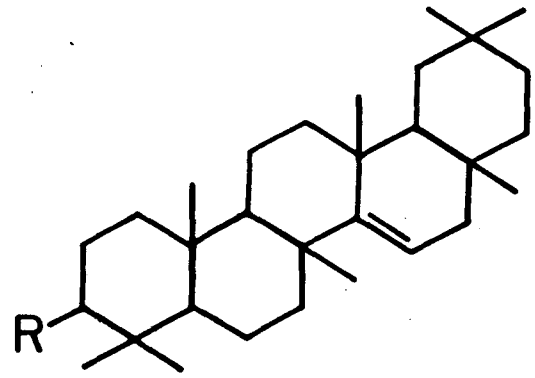
Fig. 1

a.



R = OH, or $-O-\underset{\underset{O}{\|}}{C}-(CH_2)_n CH_3$

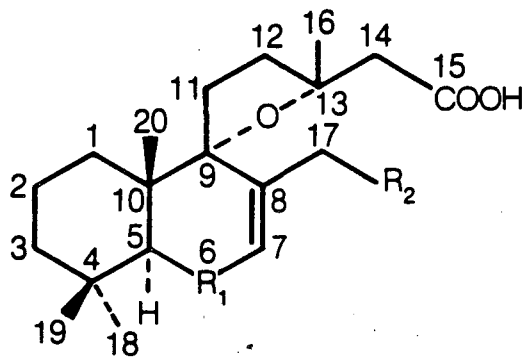
b.



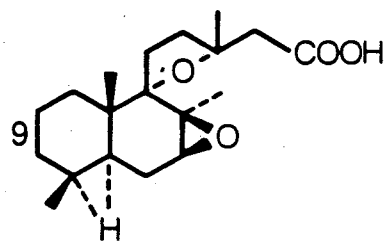
R = OH, or carbonyl

XBL 807-4260

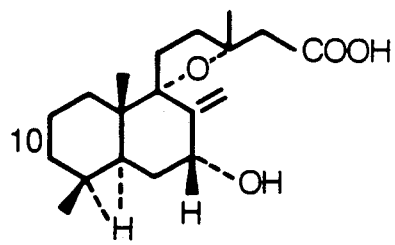
Fig. 2



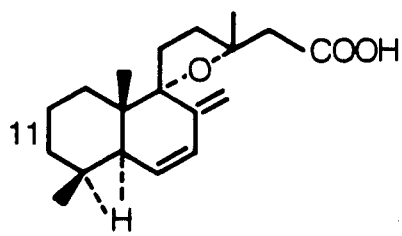
	R_1	R_1	
1	CH_2	H	grindelic acid
2	C=O	H	6-oxo-grindelic acid
3	CHOH	H	6-hydroxy grindelic acid
4	CH_2	OMe	17-methoxy grindelic acid
5	CH_2	OCOMe	17-acetoxy grindelic acid
6	CH_2	$OCOCH_2Me$	17-propionyloxy grindelic acid
7	CH_2	$OCOCH(Me)_2$	17-isobutyryloxy grindelic acid
8	CH_2	$OCOCH_2CH(Me)_2$	17-isovaleryloxy grindelic acid



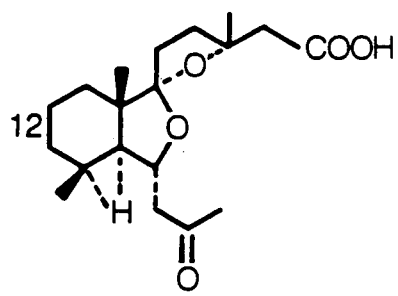
7a,8a,-epoxy grindelic acid



7-hydroxy-8(17)-dehydro grindelic acid



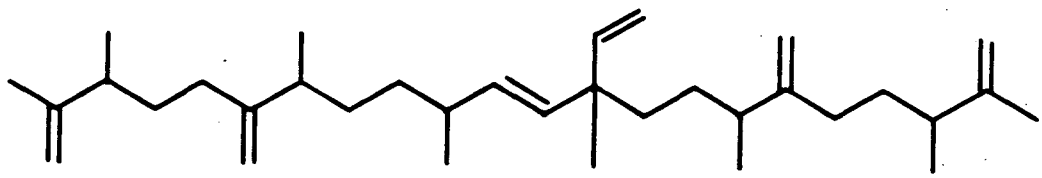
6,8(17)-diene grindelic acid



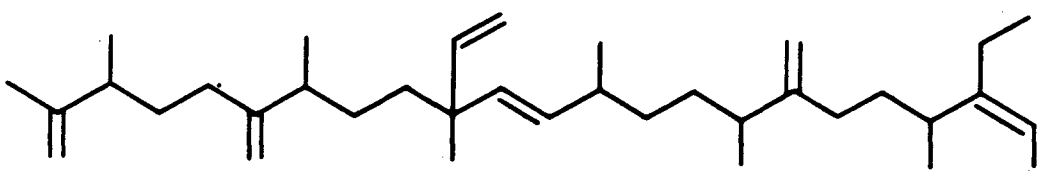
strictanonoic acid

Fig. 3

XBL8310-599



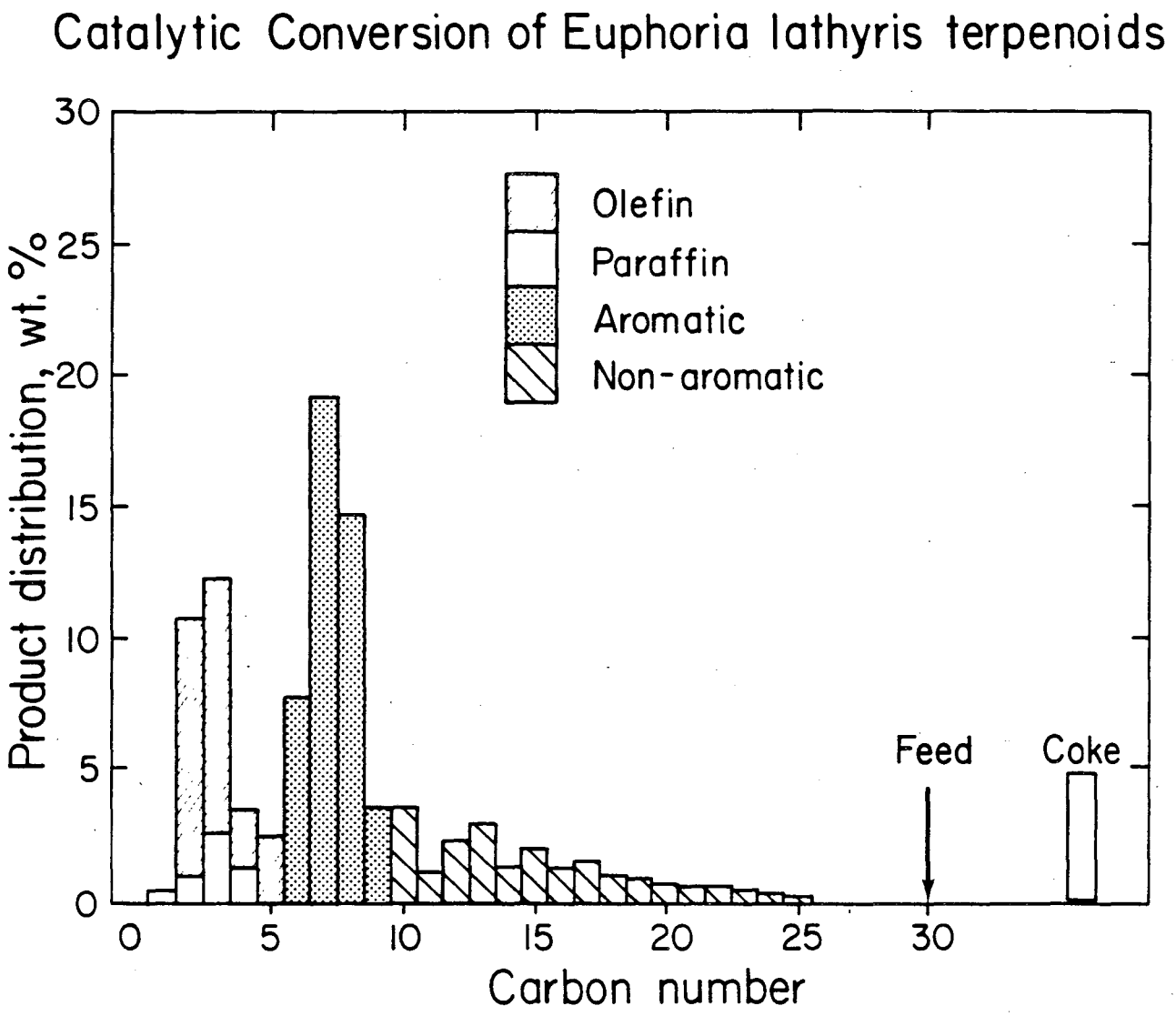
botryococcene



darwinene

XBL8310-600

Fig. 4



XBL807-4261A

Fig. 5

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720