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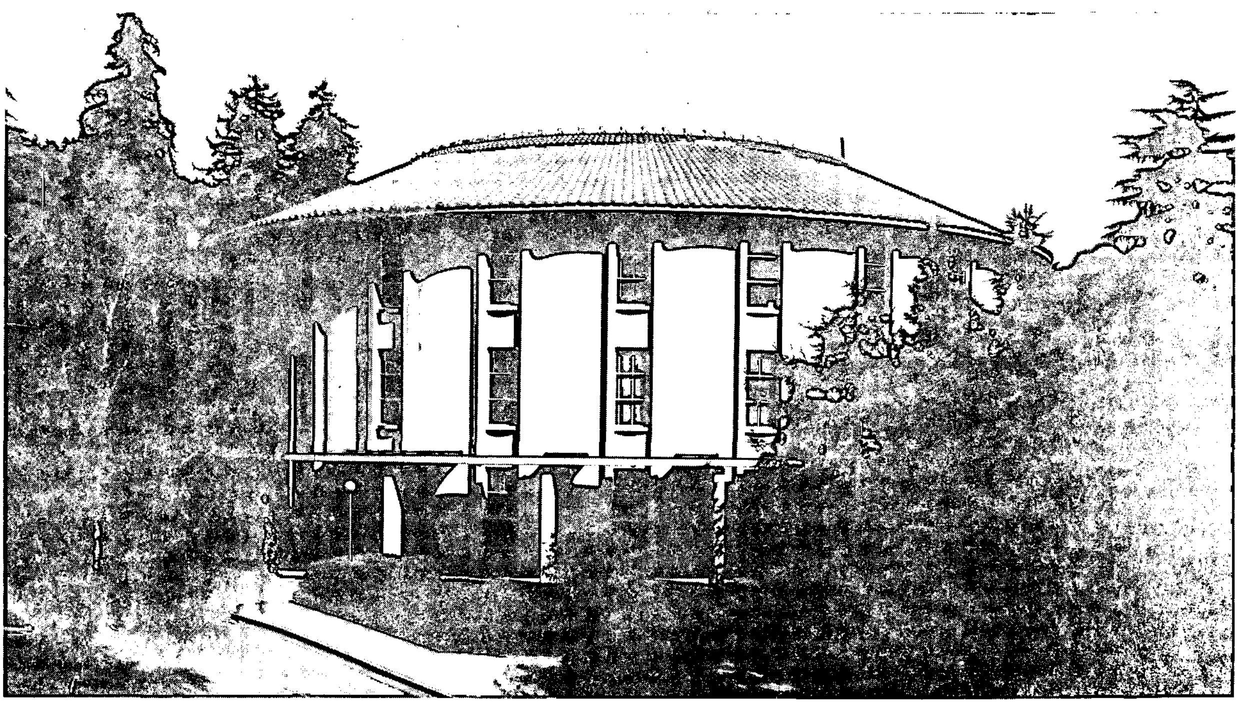

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DISCLAIMER

FUEL OILS FROM HIGHER PLANTS

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Abstract

All green plants produce carbohydrates as a first product in the reduction of CO_2. These are half-way up the energy scale from CO_2 to hydrocarbon. Some plants, however, are capable of carrying the transformation further into hydrocarbon oil. It is in the selection and modification of these latter steps that we will achieve the continuous replacement of the higher energy containing chemicals upon which modern society is dependent.

In addition to the seed oils, which exemplify the biosynthetic process of reducing carbohydrate to hydrocarbon, there exist a number of plant families in which this is done to a varying degree. In the Euphorbiaeceae family, the genus Euphorbias produces a latex composed of about 30% triterpenoid material. One of the more common is the "gopher plant", Euphorbia lathyris. Representatives of another plant family, the Asclepiadaceae, produce similar materials and the more common are called milkweeds. Both the Euphorbias and Asclepias are annual herbaceous plants which must be cut, dried and extracted. They produce about 8% of their dry weight as an oil and 20% of the dry weight is fermentable sugar, the rest being lignocellulose.

A more promising approach for renewable fuels and materials is one in which the plant is a tree which can be harvested annually, either by tapping or from its fruits, to produce terpenes. The most promising species is a tropical tree, belonging to the Leguminosae family, of the genus Copaifera which grows in tropical lands such as Amazonas in Brazil. It is possible to tap the Copaifera multijuga in a manner similar to that used for sugar maples. The tapping produces about 25 liters of a mixture of cyclic sesquiterpenes (diesel-like material) in a 24-hour period, twice a year.

Another group of trees produces fruits rich in terpenes. These are in the genus Pittosporum of the family Pittosporaceae. So far the most promising candidate is Pittosporum resiniferum known in the Philippines. Its fruit is the size of a prune and contains roughly 30% terpenes; it is probably capable of adaptation to more temperate climate. Another member of the same family, Pittosporum undulatum, is an ornamental plant/tree in California with fruits about 1 cm in diameter, alson containing about one-third terpenes. The tonnage yields from each of these trees per acre (or per hectare) have not yet been determined, but deserve to be since the harvest would consist almost entirely of the oil and residual lignocellulosic components of the fruit.

FUEL OILS FROM HIGHER PLANTS

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It is apparent that an alternative to fossil fuels must be found and developed. The obvious one is to use solar energy in some form. The best solar energy converting machine available is the green plant which can produce fuel and materials on an annually renewable basis. (Adams and McChesney, 1983; Buchanan, et al. 1978; Calvin, 1976, 1977, 1978a,1978b,1979b,1980,1983a,1984; Calvin, Nemethy, Redenbaugh and Otvos, 1982; Hoffman, 1983; Johnson and Hinman, 1980; Lipinsky, 1981; McLaughlin and Hoffman, 1982; McLaughlin, Kingsolver and Hoffman, 1983; Nemethy, 1984; Weisz and Marshall, 1979a)

Sugar Cane. The best green plant for converting solar energy is sugar cane. This idea of using an agricultural product, i.e., sugar cane, to provide the energy for the rest of agriculture is not new. It was promulgated many years ago in various forms, but in recent times its most important protagonist has been Brazil, one of the largest sugar producing countries in the world. (Yang, Trindade and Castello-Branco, 1981) Most of you are aware that the Brazilians began a "sugar cane for fuel" effort about 1975 when a tax program was instigated which would permit the construction of autonomous alcohol plants, that is, plants that produce only alcohol, no sugar. The sugar cane is harvested and only alcohol is produced from the juice.

The productivity of fermentation alcohol from molasses in Brazil in 1975 was nly from molasses 700 million liters. In 1983 the productivity as a result of the new program was over 5 billion liters of fermentation alcohol from sugar cane, and in 1984 the rate was about 7 billion liters. The Brazilians are producing more than 20% of their total liquid energy needs from alcohol. In Brazil they are now beginning to discuss the creation of a chemical industry based on this liquid energy; they want to call it a sucrochemical industry.

The process in the autonomous alcohol plants is as follows: There is enough steam produced in the Brazilian sugar mills to have excess electricity which can either be sold to the grid, and the money used to purchase fertilizer (ammonia) or, in isolated areas, the excess electricity can be used in small hydrogen or ammonia generators to produce the fertilizers required for the plantation. Steps have been taken to improve the heat values obtained from the bagasse, such as pelletizing the bagasse which also produces a high temperature. Becauase it is pelletized at high temperature, the lignin and waxes of the bagasse come to the surface of the pellets. The pellets can be used directly as a fuel in either coal oroil burning furnaces, instead of burning the bagasse. This method gives rise directly to electric pwoer production which is not required for the agricultural process(es) and wh ich can distributed by the grid.

In Puerto Rico there has been a development to improve the sugar cane itself. An examination was made of the clones of sugar cane wh ich had been developed, clones which had been rejected as not being good enough for sugar production becausae the content was only 7 to 9 per cent. The advantage of the "energy cane" was that it grew much larger than the preferred sugar cane (Gran cultura) which contains 14 per cent sugar. The net result has been the development of two separate types of cane in Puerto Rico, Gran cultura cane and "energy cane" (FIGURE 1). (Alexander, 1980). It is possible to obtain as much sugar from energy cane per hectare as from ordinary cane, but three times as much bagasse is produced, making the total energy production roughly three times that of the Gran cultura. The Puerto Ricans are planning to use the energy cane as a raw material for feeding large power plants. The energy cane was not useful for sugar alone because it was necessary to process three times the mass of bagasse for the amount of sugar, but when the bagasse became useful in a power plant, the growing of "energy cane" became effectively economic.

Seed Oils. There are some green plants which do not stop with the production of carbohydrate, but which continue the biosynthetic process to reduce the carbohydrate to hydrocarbon. This process is exemplified in the seed oils. (Adams and Seiler, 1984;Doty, 1984; Princen, 1982,1984; Pryde, 1984; Schultz and Morgan (1984) Some seed oils, such as sunflower, can be used directly in farm machinery engines in the same way that diesel oil is used. Most seed oils are triglycerides and are not very useful as a diesel fuel directly. However, they can be used in several ways, one of which is simply to add the seed oil(s) to the diesel fuel as a diluent. A much better way, which is now being developed for seed oils in the United States, is to transesterify the seed oil with methyl alcohol, that is, take the triglyceride, treat it with methyl alcohol and an acid catalyst which can be added as an acid ion exchange resin. Ester exchange occurs, resulting in glycerine at the bottom and the methyl esters on the top. These two substances can be separated easily and the methyl esters mixture can be used directly as a diesel fuel. This same process can be used with any type of triglyceride seed oil if it is cheap enough. Seed oils can also be hydrogenated so that unsaturation can be used and the polymerization in the engines stopped.

Vegetable oils for diesel fuels have a number of advantages (FIGURE 2). They are liquid, from renewable resources and have a favorable energy input/out ratio. They would permit energy crop production, even in an petroleum shut-off situation and also have the potential for making marginal lands productive. They consume less energy than alcohol production, have a higher energy content than alcohol, have cleaner emissions and simpler technology. At present, vegetable oils for fuel are not economically feasible, partly for the reason that on-farm process technology has not yet been completely developed. In addition, the price of the glyceride is too high and the price of diesel is too low. The dollar balance at the moment (March 1985) requires an input of $106.90 [for 530 lbs of glyceride ($99) and 96 lbs of methanol (7.91)]. The total output would be $112.30 (not counting any processing costs) produced by 269 lbs of methyl ester (equivalent of diesel) valued at $32.30 and 94 lbs of glycerine whose value is $80.00.

The best commercial seed oil is palm which is grown on a large scale in Malaysia and Brazil. Table 1 gives the oil content and average oil yield for seed oil crops in various parts of the world, and there is no question that palm oil is the most important. Palm oil can be separated by high pressure liquid chromatography into various components, each of which can be used for some definitive purpose. Palm oil yields have been increased by cloning to make this an even more important source of liquid energy and materials. (Padley, 1984).

Table 1

Oil Content and Average Oil Yield for Some Seed Oil Crops

Oil Crop (Location)	Oil Content wt %	Average Oil Yield kg/ha
Palm oil (Malaysia)	20	3,475
Copra (Philippines)	65-68	800
Peanuts (U.S.)	45-50	790
Safflower (U.S.)	30-35	762
Sunflower (U.S.)	40-45	589
Rapeseed (Canada)	40-45	409
Soybean (U.S.)	18-19	319
Corn kernel (U.S.)	4.8	254
Flaxseed (U.S.)	35-42	230
Sesame (India)	45-50	220
Cottonseed (U.S.)	18-20	140

Herbaceous Plants. There are also plants which take the initially produced carbohydrate and instead of converting it into fatty acids and glycerides (such as the seed oils) convert it into terpenes. (Nemethy, 1984; Nielsen, et al. 1977; Buchanan, et al. 1978; Calvin, 1983, 1984; Calvin, Nemethy, Redenbaugh and Otvos, 1982; Hoffman, 1983; Lipinsky, 1981, McLaughlin, Kingsolver and Hoffman, 1983) The presently most important commercial plant of this type is *Hevea brasiliensis*, a member of the *Euphorbiaeceae* family, which makes polyisoprene rubber; this tree is grown extensively in Malaysia, Indonesia and The Philipppines. There are other members of the Euphorbiaeceae family that produce hydrocarbons, especially the genus called Euphorbia which has 2000 species of all sizes which grow throughout the world. Every single one of the Euphorbias produces a latex which is an emulsion of roughly 30 per cent terpenes in water. The latex is largely a C_{30} triterpenoid which can be cracked like oil to make high octane gasoline. (Weisz and Marshall, 1979b) One such plant Euphorbia lathyris, grows in California and many other places in the world (FIGURE 3) and was the first hydrocarbon-producing plant studied to test the hypothesis that plants could be grown for fuel and chemical content in marginally suitable land. (Calvin, 1977, 1979b). The entire E. lathyris plant is harvested, and from that harvest 8 per cent of the dry weight of the plant is extracted as terpenes (oil), 20 per cent of the dry weight is fermentable sugar, which leaves about 30 per cent as lignocellulose which can be used in a way similar to the bagasse of sugar cane, or, better yet, compressed into more efficiently burning pellets. From E. lathyris it is possible to obtain three products: terpenes, which are an oil and which can be cracked like crude oil; fermentable hexoses, which can be fermented like sucrose, and lignocellulose. (Nemethy, Otvos and Calvin, 1979, 1981a,b). The products of the extraction of the Euphorbia lathyris represent a new possibility for a future energy and materials source.

The zeolite catalyst cracking of the crude oil from the Euphorbia lathyris resulted in the usual group of products which are similar to those from standard cracking of petroleum, such as olefins, paraffin, aromatics and nonaromics. This information confirms the desirability of the products of E. lathyris as possible raw materials to substitute for crude oil. As a result of additional data on processing and cracking the material from E. lathyris it now appears that a price of $100/barrel for the oil would be realistic. This is still within reason, considering that it is only about twice as much as the current price/barrel for crude from OPEC.

Euphorbia lathyris plantations have been developed in various parts of the world, and in Spain at the experiment station near Madrid as much as 9000 kilos/hectare of plant material can be obtained, with the average being about 5000 kilos/hectare even without irrigation and fertilization. (Ayerbe, et al, 1984).

Other plants besides Euphorbias contain the same kind of latex, one of the most important being the milkweeds, a member of the Asclepiadaeceae family. The largest plantation of milkweeds (Asclepias speciosa) in the world is located outside Salt Lake City, Utah (FIGURE 4) and the yields of this species are of the same order of magnitude as for the E. lathyris (Adams, 1984van Emon and Seiber, 1985) Another member of the Asclepiadaceae family which is being cultivated on plantations in the United States, Puerto Rico and Australia is Calotropis procera which also has about the same distribution of oil-sugar-lignocellulose as the Euphorbias. (Carruthers, et al. 1984; Erdman and Erdman, 1981; Erdman, Gregorski and Pavlath, 1984; Peoples and Lee, 1982) A comparison of energy yields for different crops is shown in Table 2. It is clear that the most important component in the table is the energy in liquid fuels as hydrocarbons in millions of Btus per acre per year per inch of water. There is no question that it would be possilble to introduce into the United States as well as certain

Table 2

Comparison of Energy Yields for Different Crops

PROCESS	DRY BIOMASS YIELD TONS $ACRE^{-1} YR^{-1}$	LIQ. FUEL YIELD/ACRE YR^{-1}	WATER REQ. IN. YR^{-1}	ENERGY IN LIQ. FUEL (10^6 BTU) $ACRE^{-1} YR^{-1}$ PER INCH OF WATER	CELLULOSIC RESIDUE $ACRE^{-1}$ YR.	ENERGY IN CELLULOSE (10^6 BTU) PER ACRE YR^{-1} PER INCH
CORN TO ETHANOL	5	16×10^6 BTU (0.64 tons)	25	0.65	44.2×10^6 BTU (3.4 tons)	1.77
SUGAR CANE TO ETHANOL	30	60×10^6 BTU (2.4 tons)	78	0.78	312×10^6 BTU (24 tons)	4
ENERGY CANE TO ETHANOL	35 - 50	65×10^6 BTU (2.56 tons)	48	0.35	400×10^6 BTU (31 tons)	8.2
EUPHORBIA LATHYRIS TO HYDROCARBON AND ETHANOL	8.5	20×10^6 BTU (0.58 tons) 17.3×10^6 BTU (0.68 tons)	25	0.82 0.78	79.6×10^6 BTU (6.12 tons)	3.2
PITTOSPORUM RESINIFERUM (FRUIT ONLY) to HYDROCARBONS	7.8	50×10^6 BTU (1.5 mtons)	~25	2.0	101×10^6 BTU (7.8 mtons)	4.0
JATROPHA CURCAS (SEED ONLY) to HYDROCARBONS	5.0	92×10^6 BTU (2.2 mtons)	~25	3.6	36×10^6 BTU (2.8 mtons)	1.45
PALM (Fruit)	8.1	73×10^6 BTU (1.8 mtons)	(~25)	(2.9)	(~1 mton)	

other countries a substantial energy agriculture were the economic inentives for such biomass production of the right type.

The extraction process for all the oil-producing plants for a 1000 dry tons per day plant yields 80 tons of oil and 200 tons of fermentable sugar, which would correspond to the 20 per cent sugar and 8 per cent oil in the dried plant. This process is similar to that for vegetable oil extraction, can be done on a very small scale and could be utilized by farmers' cooperatives for oil extraction of energy-type crops. A cost estimate of a relatively small processing pilot plant for herbaceous crops, based on Euphorbia lathyris, is shown in Table 3.

While it is possible to use some plant hydrocarbons directly as transportation, and even seed oils (mostly triglycerides) have been tested as diesel substitute, the viscous, often solid whole plant extracts of latex-bearing plants need to be upgraded for liquid fuel use. This can be done by a modified shape selective zeolite catalyst process developed by Mobil Research Company to produce gasoline and aromatics from plant extracts. (Weisz and Marshall, 1979b)

Hydrocarbon Producing Trees. One of the problems with using annual herbaceous plants as a source of hydrocarbons is soil erosion. It would be better agronomic practice to grow trees for energy-rich products and either harvest the fruit or tap the tree for oil, in which case the soil would not be disturbed each year. A number of trees, such as eucalyptus, exist which can produce hydrocarbon products. For example, the fruits and leaves of eucalyptus can be harvested and steam distilled to obtain a mixture of terpenes. From the Eucalyptus globulus about ten or twelve terpenes are obtained of C_{10} construction, followed by C_{15} sesquiterpenes. (Nishimura and Calvin, 1979) This very complex mixture

Table 3

COST ESTIMATE FOR *EUPHORBIA LATHYRIS* PROCESSING PILOT PLANT

ACREAGE:	3000 acres	10 tons/acre	100 tons/day	8 tons oil	∿ 48 barrels
				20 tons sugar (@5¢/pound)	∿ 60 barrels

COSTS (ANNUAL)		
Farming	$ 900,000	@$300/acre or $30/ton
Financing (1M @10%)	100,000	Average 10% interest/year for 10 years
Depreciation	100,000	Return of capital
Labor: 5 x $30,000	150,000	
Total costs	$1,250,000	

INCOMES (ANNUAL)	Minimum (1985)			Maximum (1985)		
Oil	30 bbls	$30 x 365	$ 328,500	40 bbls	$30 x 365	$ 438,000
Alcohol equivalent	40 bbls	$62 x 365	$ 905,000	50 bbls	$62 x 365	1,132,000
Total costs			$1,233,000			$1,510,000

(plus value of 20 tons/day bagasse)

(50 tons/day burned for process heat)

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of terpenes from eucalyptus could be cracked for gasoline or used in other ways.

Another species of tree has been studied for its terpene production. This is the Pittosporum resiniferum, a member of the Pittosporaceae family which grows in The Philippines. The fruit from the tree is rich in light oil (FIGURE 5). The unripe fruit burns brilliantly when ignited and some people use the "petroleum nuts" for fuel. This tree is being explored in The Philippines as an oil source, and plantations have been started with the fruits being harvested and extracted for their oil content on an experimental basis. (Fernandez, private communication). The results indicate that the fuel properties of the steam distilled oil from the P. resiniferum fruits after hydrogenation are quite comparable with those of gasoline. The plans are to test the oil in engines as soon as enough is available. The major components of the oil, based on gas chromatographic analysis, are α-pinene (33 per cent), β-pinene (24 per cent) and heptane, with lesser amounts of limonene and myrcene. (Nemethy and Calvin, 1982).With the P. resiniferum we can assume an average of 20 per cent oil yield and a maximum yield of 18 kg of fruits/tree/year at a high density planting. A maximum oil yield/acre/year would be 10 barrels, and with smaller fruits the yield would be approximately 6.5 barrels/acre/year. This species appears to be a very desirable fuel crop if high-yielding trees an be selected and planted at high density.

Another species, Pittosporum undulatum grows prolifically in California and the fruits have also been analyzed for the terpene content. These fruits are smaller than those of the Philippine tree, and when they were extracted they were found to have the same terpenes (C_{10}

compounds). Because this genus does grow well in various parts of the world, The Pittosporum may turn out to be good candidates for terpene production.

Still a third tree which is an excellent candidate for biocrude production is located in Brazil, in the same environment as the Hevea rubber tree. It is a species of Copaifera (Leguminosae family) and can be tapped for oil. (Alencar, 1982; Langenheim, 1981). The trunk of the Copaifera multijuga tree is quite large, and a wooden bung is inserted into a hole which has been drilled horizontally into the trunk of the tree into the heartwood. As the bung is removed, the oil begins to run out into a container and it can be used directly in a diesel engine without any further purification. (Calvin, 1980, 1982) The oil is a very complex mixture of sesquiterpenes, (Arrhenius, et al, 1983). The main components of the Copaiba oil, as it is commonly called, are carophyllene, bergatomene and copaene, all cyclic C_{15} compounds. (Wenninger, Yates and Dolinsky (1967). The oil from the C. multijuga has also been subjected to the Mobil zeolite catalyst process and the results indicate that it can be cracked into a useful suite of compounds similar to those found in Euphorbia lathyris.

Biosynthetic Pathways. The terpenes in hydrocarbon-producing plants and trees are probably made by a well kown biosynthetic pathway: Sugar to pyruvic acid to mevalonic acid to isopententylpyrophosphate (IPP). The double bond IPP is isomerized to make dimethylallylpyrophosphate (DMAP, and the two isomers combine. The allylic phosphate comes off DMAP and the resulting carbonium ion attacks the double bond of IPP, followed by proton loss, which results in exactly the same allylic structure as before. Eventually, if the process continues, rubber is the result.

A comparison of biosyntheic routes might be of interest here. In the case of Euphorbia lathyris the sequence is all the way to C_{15} compounds, with dimerization to C_{30} followed by cyclization. In the Pittosporum, however, the route is to the C_{10} compounds followed by cyclization to create monoterpenes in the fruit. The biosynthetic method by which the diesel oil from the Copaifera is made is the same as that used by the E. lathyris up to the C_{15} step. The Copaifera cyclizes the C_{15} farnesyl pyrophosphate, that is, drops the phosphorus off to give the cyclic C_{15} compounds. One type of enzyme is responsible for the difference in the two end products of C. multijuga and E. lathyris and that is the farnesyl pyrophosphate cyclase enzyme. With Euphorbia lathyris this compound is dimerized while with the Copaifera the material is cyclized with many cyclic C_{15} products as a result.

OIL PRODUCTION BY ALGAE

There is one other means of "growing oil" and that is to use a unicellular algae which will produce that oil.(Bachofen, 1982) (FIGURE 6) One such algae is Botryococcus braunii, a fresh-water species which produces terpenoid oils. (Wolf, 1983) Colonies of this alga are often observed floating on the surface of undisturbed waters. This buoyancy is the result of the large amounts of accumulated oil in the alga. In the so-called resting state the Botryococcus has been reported to produce as much as 86 per cent of dry weith as oil, although a more typical range of oil concentration is 25 to 40 per cent. (Brown, Knights and Conway, 1969; Wake and Hillen, 1981). 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.The series encompasses linear isoprenoids from C_{30}

to C_{37}. The structure of the C_{34} compound, name Botryococcene, has been elucidated, (Cox, et al. 1973), and more recently the structure of the C_{36} compound, named "Darwinene", has been reported. (Galbraith, Hillen and Wake, 1983). 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. (Wolf, et al., in press). It is unique among alga in its ability to synthesize and accumulate high levels of hydrocarbons which are suitable for feedstock material or liquid fuels. Hydrocracking of the Botryococcus derived oil yielded 62 per cent petroleum, 15 per cent aviation fuel, 15 per cent diesel fuel and 3 per cent heavy oil. (Hillen, et al. 1982).

CONCLUSION

The use of plants for fuel is not a new idea. Two different efforts were made over 40 years ago in this direction. The first was an attempt by the Italians in Ethiopia to use a member of the Euphorbiaeceae family, E. Abyssinica, as a source of fuels (Frick, 1935). These plants grow prolifically in Ethiopia and the Italians proposed to build an extraction plant for the oils from these plants, but they had to abandon the effort when they left Ethiopia in 1938. The French in Morocco in 1940 used E. resiniferum as a possible oil source and did obtain oil from the wild plants; the yield was 3 metric tons of oil/hectare from wild plants. However this effort also was not continued. (deSteinheil, 1941).

The idea of using plants to create hydrocarbon-like materials as a substitute for fuel and materials will become more important, especially in some of the less developed areas of the world which have a great deal of land not very suitable for food production. Various efforts have been made in Spain, Okinawa, Thailand and Australia, and attempts are underway to improve agronomic yields, develop small scale extraction plants and learn more about the composition of the oil itself.

What is needed now is an effort on the part of the agricultural community to commit itself to an "energy agriculture" which would have long term benefits for the world. It is my feeling that we will probably have to be shown by others that this type of development is feasible. Nevertheless, the projections for energy use in the United Sttes for the year 2000 for the first time include biomass as a significant component of the total, representing about 6 per cent of the energy requirement. One way to encourage the development of biomass would be to have farmers set aside a part of their land to "grow" a plant which produces a fuel of the correct type, such as seed oils, to run their agricultural machinery. This would be a return to the practice of one hundred years ago when farmers used part of the farm to produce the energy needed, mostly as carbohydrate (grass) for work-animal feed.

Ultimately a totally synthetic device will be developed for the conversion of solar quanta into chemical form, completely independent for the need for arable land. This process, which I have called artificial photosynthesis, (Calvin, 1978c, 1979a, 1983) is aimed at mimicking nature's photosynthetic apparatus by devising an artificial system of chemicals and components which is capable of storing the free energy of visible light in the form of chemical free energy. The chemical form of the components and their physical arrangements are suggested by what we have learned bout the details of the natural process, namely, the phototransfer of an electron across a phase boundary, but are not limited in choice of materials by what is found in natural photosynthetic units.

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REFERENCES

Adams, R. P. (1984). The showy milkweed Asclepias speciosa: A potential new semi-arid land crop for energy and chemicals. Biomass 4, 81-204.

Adams, R. P. and McChesney, J. D. (1983). Phytochemicals for liquid fuels and petrochemical substitutions: Extraction procedures and screening results. Econ. Bot. 37, 205-215.

Adams, R. P. and Seiler, G. J. (1984). Whole-plant utilization of sunflowers. Biomass 4, 69-80.

Alencar, J. (1982). Estudos silviculturais de uma populacae natural de Copaifera multijuga Leguminosae na Amazonia centra. 2. Producao de oleo resena. Acta Amazonia 12, 75-89.

Alexander, A. G. (1980). The Energy Cane Concept and Boiler Fuel. San Juan, Puerto Rico.

Arrhenius, S. P., Foster, C. E., Edmonds, C. G. and Langenheim, J. H. (1983). Sesquiterpenes in leaf pocket resins of Copaifera species. Phytochemistry 22, 471-472.

Ayerbe, L., Tenorio, J. L., Ventas, P., Fuenes, E. and Mellado, L. (1984). Euphorbia lathyris as an energy crop. Part II. Hydrocarbon and sugar productivity. Biomass 4, 37-42.

Bachofen, R. (1982). The production of hydrocarbons by Botryococcus braunii. Experientia 38, 47-49.

Brown, A. C., Knights, B. A. and Conway, E. (1969). Hydrocarbon content and its relationship to physiological state in the green alga Botryococcus braunii. Phytochemistry, 8, 543-547.

Buchanan, R. A., Cull, I. M., Otey, F. H. and Russell, C. R. (1978). Hydrocarbon and rubber producing crops. Econ. Bot. 32, 131-145, 146-153.

Calvin, M (1976). Photosynthesis as a resource for energy and materials. Photochem. Photobiol. 23, 425-444.

Calvin, M. (1977). Hydrocarbons from plants. Energy Res. 1, 299-327.

Calvin, M. (1978a). Green factories. Chem. Eng. News, 50(12), 30-36.

Calvin, M. (1978b). Chemistry, population, resources. Pure Appl. Chem. 50, 407-425.

Calvin, M. (1978c). Simulating photosynthetic quantum conversion. Acct. Chem. Res. 11, 369-374.

Calvin, M. (1979a). Synthetic chloroplasts. Energy Res. 3, 73-87.

Calvin, M. (1979b). Petroleum plantations for fuel and materials. BioScience, 29, 533-538.

Calvin, M. (1980). Hydrocarbons from plants: Analytical methods and observations. Naturwissen. 67, 525-533.

Calvin, M. (1983a). New sources for fuel and materials. Science, 219, 24-26.

Calvin, M. (1983b). Artificial photosynthesis: Quantum capture and energy storage. Photochem. Photobiol. 37, 349-360.

Calvin, M. (1984). Renewable fuels for the future. J. Appl. Biochem. 6, 3-18.

Calvin, M., Nemethy, E. K., Redenbaugh, K., and Otvos, J. W. (1982). Plants as a direct source of fuel. Experientia, 38, 28-32.

Carruthers, J. B., Griffiths, D. G., Howe, V., and Williams, L. R. (1984). Hydrocarbons from Calotropis procera in Northern Australia. Biomass 4, 275-282.

Cox, R. E., Burlingame, A. L., Wilson, D. M., Eglinton, G. and Maxwell, J. R. (1973). Botryococcene-a tetramethylated acylic triterpenoid of algal origin. J.C.S. Chem. Comm. 284-285.

deSteinheil, P. (1941). L'Euphorbe resinifere, plante a caoutchouc et resine vernis. Rev.. Gen. Caoutch. 18(2), 55-57.

Doty, H. O., Jr. (1983). Economics of oilseed production. Econ. Bot. 37, 434-443.

Erdman, M. D. and Erdman, B. A. (1981). Calotropis procera as a source of plant hydrocarbons. Econ. Bot. 35, 467-472.

Erdman, M. D., Gregorski, K. S. and Pavlath, A. E. (1984). Fuel characteristics and pyrolysis studies of solvent extractables and residues from the evergreen shrub Calotropis procera. Trans. A.S.A.E. 27, 1186-2289.

Frick, G. A. (1935). A new brand of gasoline. Cact. Succulent J. 10(9), 60.

Galbraith, M. N., Hillen, L. W. and Wake, L. V. (1983). Darwinene: A branched hydrocarbon from a green form of Botryococcus braunii. Phytochemistry 22, 1441-1443.

Hillen, L. W., Pollard, G., Wake, L. V. and White, N. (1982). Hydrocracking the oils of Botryococcus braunii to transport fuels. Biotechnol. Bioeng. 24, 293-

Hoffman, J. J. (1983). Arid land plants as feedstocks for fuels and chemicals. CRC Crit. Rev. Plant Sci. 1, 95-116.

Johnson, J. D. and Hinman, C. W. (1980). Oils and rubber from arid land plants. Science 208, 460-464.

Langenheim, J. H. (1981). Terpenoids in the Leguminosae.17. Advances in Legume Systematics (ed. R. M. Polhill and P. H. Raven) pp 627-655. Royal Botanic Gardens, Kew, Surrey, England.

Lipinsky, E. S. (1981). Chemicals from biomass: petrochemical substitution options. Science 212, 1465-1471.

McLaughlin, S. P. and Hoffman, J. J. (1982). Survey of biocrude-producing plants from the Southwest. Econ. Bot. 36, 323-339.

McLaughlin, S. P., Kingsolver, B. E. and Hoffman, J. J. (1983). Biocrude production in arid lands. Econ. Bot. 37, 150-258.

Nemethy, E. K. (1984). Biochemicals as an energy resource. CRC Crit. Rev. Plant Sci. 2, 117-129.

Nemethy, E. K. and Calvin, M. (1982). Terpenes from Pittosporaceae. Phytochemistry 21, 2981-2982.

Nemethy, E. K., Otvos, J. W. and Calvin, M. (1979). Analysis of extractables from one Euphorbia. J. Amer. Oil Chem. Soc. 55, 957-960.

Nemethy, E. K., Otvos, J. W. and Calvin, M. (1981a). Hydrocarbons from Euphorbia lathyris. Pure Appl. Chem. 53, 1101-1108.

Nemethy, E. K., Otvos, J. W. and Calvin, M. (1981b). Natural production of high-energy liquid fuels from plants. In Fuels from Biomass and Wastes (ed. D. L. Klass and G. H. Emert), pp 405-419. Ann Arbor Sci. Press, Michigan.

Nielsen, P. E., Nishimura, H., Otvos, J . W. and Calvin, M. (1977). Plant crops as a source of fuel and hydrocarbon-like materials. Science 198, 942-944.

Nishimura, H., and Calvin, M. (1979). Essential oil of Eucalyptus globulus in California. Agric. Food Chem. 27, 432-435.

Padley, F. B. (1984). New developments in oils and fats. Chem and Ind. 788-792.

Princen. L. H. (1982). Alternate industrial feedstocks from agriculture. Econ. Bot. 36, 302-312.

Princen, L. H. (1983). New oilseed crops on the horizon. Econ. Bot. 37, 478-492.

Pryde, E. H . (1984). Chemicals and fuels from commercial oilseed crops. In Fuels and Chemicals from Oil Seeds, pp. 51-69. Westview Press, Boulder, Colorado.

Schultz, E. G. Jr., and Morgan, R. P. (eds). (1984). Fuels and Chemicals from Oil Seeds: Technology and Policy Options. AAAS Selected Symp. 91. Westview Press, Boulder, Colorado.

van Emon, J. and Seiber, J. N. (1985). Chemical constituents and energy content of two milkweeds: *Asclepias speciosa* and *A. curassavica*. Econ. Bot. 39, 47-55.

Wenninger, J. A., Yates, R. L. and Dolinsky, M. (1967). Sesquiterpene hydrocarbons of commercial Copaiba balsam and American cedarwood oils. J. Amer. Oil Chem. Soc. 50, 1304-1312.

Weisz, P. B. and Marshall, J. F. (1979a). High grade fuels from biomass farming: Potentials and constraints. Science 206, 24-29.

Weisz, P. B. and Marshall, J. F. (1979b). Catalytic production of high grade fuel (gasoline) from biomass compounds by shape selective catalysis. Science 206, 57-58.

Wolf, F. R. (1983). *Botryococcus braunii*, an unusual hydrocarbon-producing alga. Appl. Biochem. Biotech. 8, 249-260.

Wolf, F. R., Nemethy, E. K., Blanding, J. H. and Bassham, J. A. (1985). Biosynthesis of unusual acylic isoprenoids in the alga *Botryococcus braunii*. Phytochemistry in press.

Yang, V., Trindade, S. C. and Castello-Branco, J. R. (1981). How Brazil grows motor fuel. Chemtech. 11, 168-172.

FIGURE CAPTIONS

FIGURE 1 Energy cane, Puerto Rico. (Photo by Gene Elle Calvin)

FIGURE 2 Relationship between viscosity and temperature, sunflower oil, ester and diesel fuel

FIGURE 3 *Euphorbia lathyris*, California

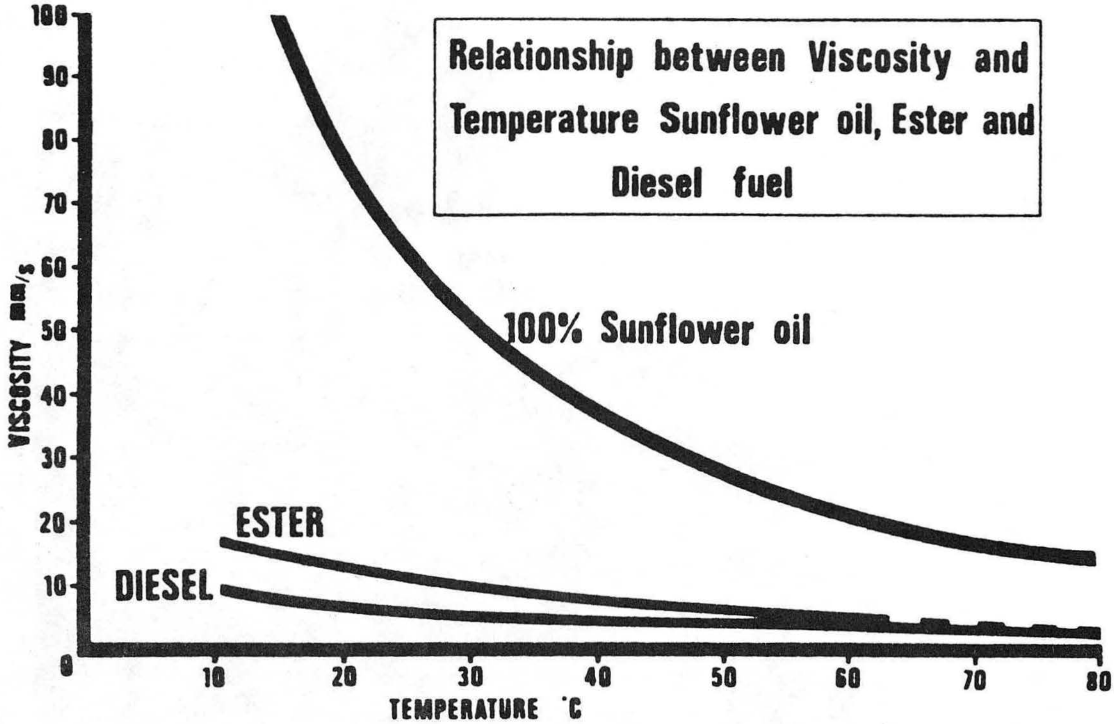
FIGURE 4 *Asclepias speciosa*, Utah

FIGURE 5 *Pittosporum resiniferum* fruits, Philippines

FIGURE 6 *Botryococcus braunii* algae showing hydrocarbon production

Fig. 1

CBB 822-1649



XBL 8412-5334

Fig. 2

Fig. 3

CBB 800-13496

Fig. 4 CBB 834-3348

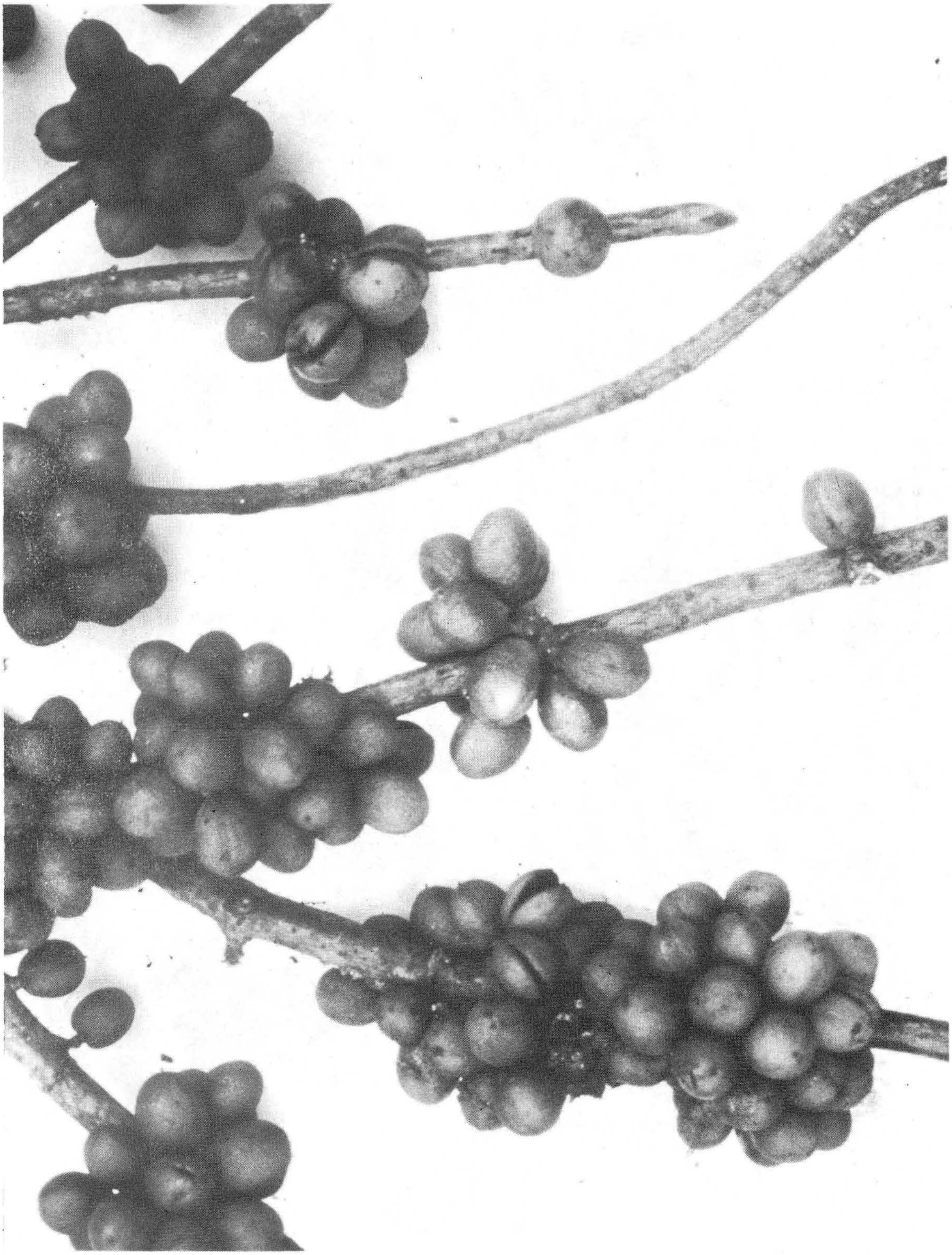


Fig. 5 CBB 852-1108

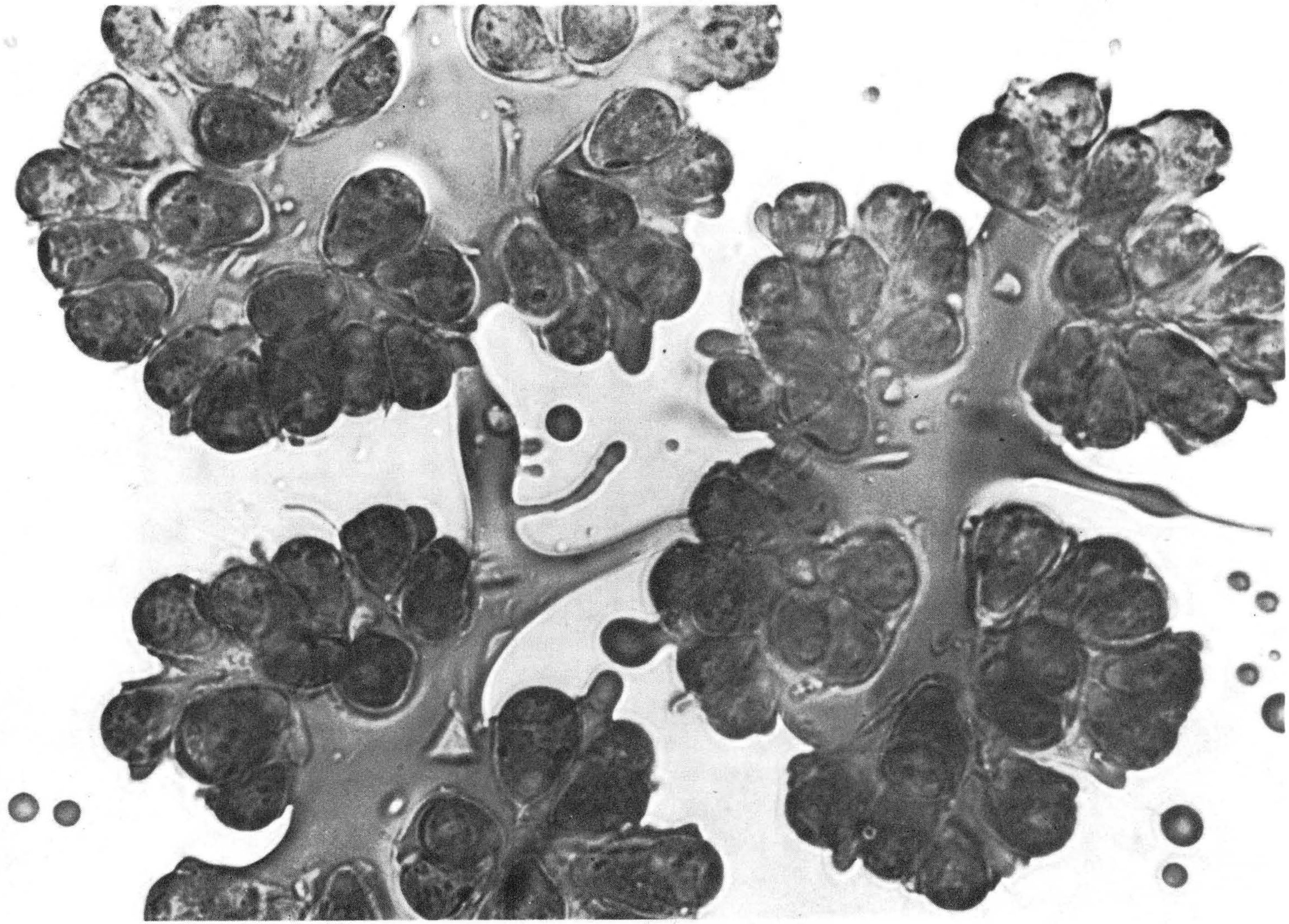


Fig. 6

CBB 835-4582

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