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April 1, 1978

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PETROLEUM PLANTATIONS

Melvin Calvin

April 1978

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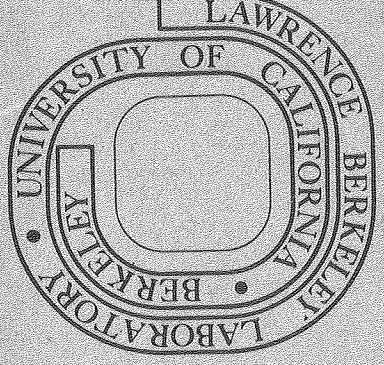

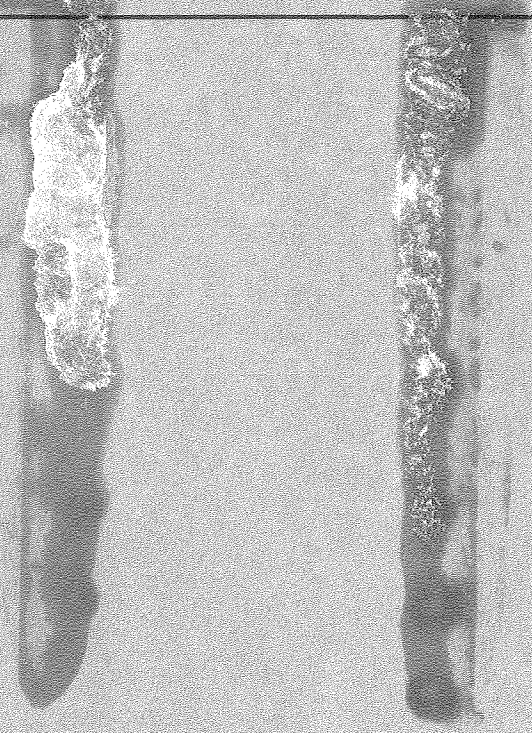

PETROLEUM PLANTATIONS*

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ABSTRACT

Photosynthesis is examined as an annually renewable resource for material and energy. The production of fermentation alcohol from sugar cane as a major source of materials for chemical feedstocks is examined as well as the direct photosynthetic production of hydrocarbon from known plant sources. Experiments are underway to analyze the hydrocarbons from Euphorbias and other hydrocarbon containing plants with a view toward determining their various chemical components. In addition, experimental plantings of several species of Euphorbias have begun to obtain data on which species would be most successful. Using Euphorbia lathyris, there are indications that we may expect a yield of approximately ten barrels of hydrocarbon material per acre in a seven-month growing period on semiarid land.

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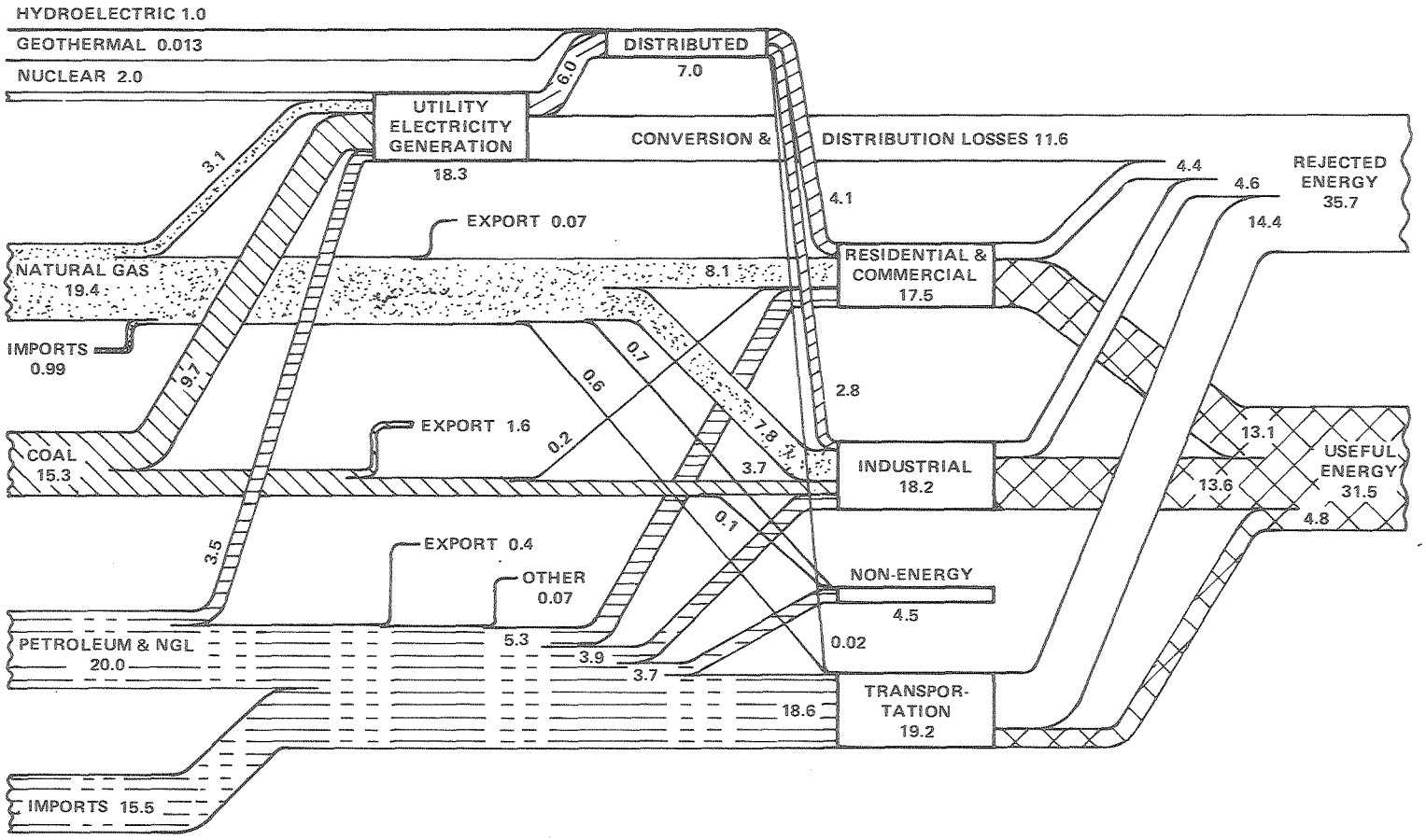
This is an application of some of our earlier work to a practical problem which we must solve in order to survive. The problem to which I refer is the problem of our energy supply, which today, for the most part, is fossil fuel.

Figure 1 shows the flow of energy in the United States in 1976. From the left side of the figure, you can see that it is largely fossilized photosynthetic product. Ninety eight percent of our energy resources, as shown on the left side of this figure, are oil, gas or coal--all three of which represent fossilized carbon that is first reduced by photosynthetic organisms.

There is no need for me to remind you of the fact that the finding and delivery of the convenient fossil fuels, oil and gas, has become an increasing

U.S. ENERGY FLOW — 1976

(PRIMARY RESOURCE CONSUMPTION 72.1 QUADS)



XBL 776-4456

problem. In our country, production is now falling. In the world, discovery is now falling. It behooves those of us who are dependent upon fossil fuel, at least in the form of oil and gas, to find some other way to fulfill our needs.

In the United States we still have a very substantial supply of fossil carbon in the form of coal, which is fossilized photosynthetic product. Figure 2 shows something of that sort: it shows that we will very soon (i.e., in the next 20 years) be completely out of oil. On the other hand, the supply of coal (represented by the lighter area of this graph) may be expected to continue for several hundred more years. Therefore, there is a considerable movement in the United States, and in the rest of the world as well, to make a greater use of coal as a source, not only of energy, but of chemical feedstocks as well. It seems to me that there are constraints on this use which will prevent us from continuing and expanding the use of coal as our principal source of energy and of chemical raw materials, even though it may be physically possible to do this.

There are two principal constraints on the expanded use of coal. The first of these is illustrated in Figure 3, in which I show the result of liquifying coal, i.e. making oil out of coal. This can be done, and the figure shows the example of one 25,000 ton/per/day plant (or factory) for converting coal into oil. You can see here that, while we will make somewhat more than 25,000 tons of oil, that oil will contain 200,000 pounds (about 100,000 kilos) of polycyclic aromatic hydrocarbons, because coal is so poor in hydrogen. In particular, this oil will contain about 10 pounds, which is about 5 kilos, of benzo(a)pyrene, which we know to be a potent carcinogenic chemical--one which is produced when any organic matter is burned but particularly when coal is used, simply because it is so poor in hydrogen. Benzo(a)pyrene is a very powerful carcinogen, and is one of the principal causes for the rise in lung cancer among smokers in my country, and I suspect

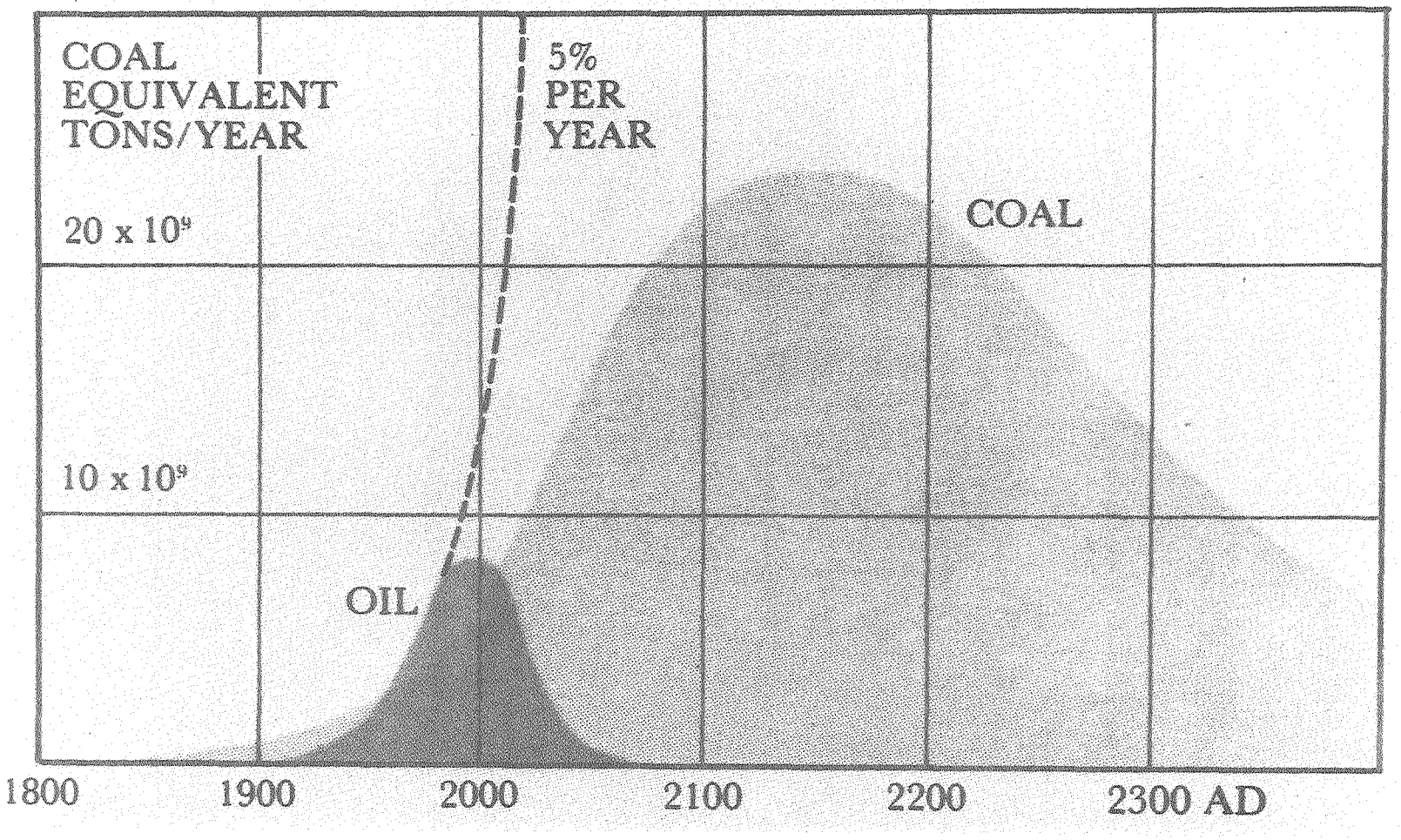


Figure 2. Oil and coal use cycles

XBB 778-7577

POTENTIAL CARCINOGEN PRODUCTION IN COAL OIL PLANT

(25,000 TONS / DAY OF COAL)

POLYCYCLIC AROMATICS - - - 200,000 lbs/day

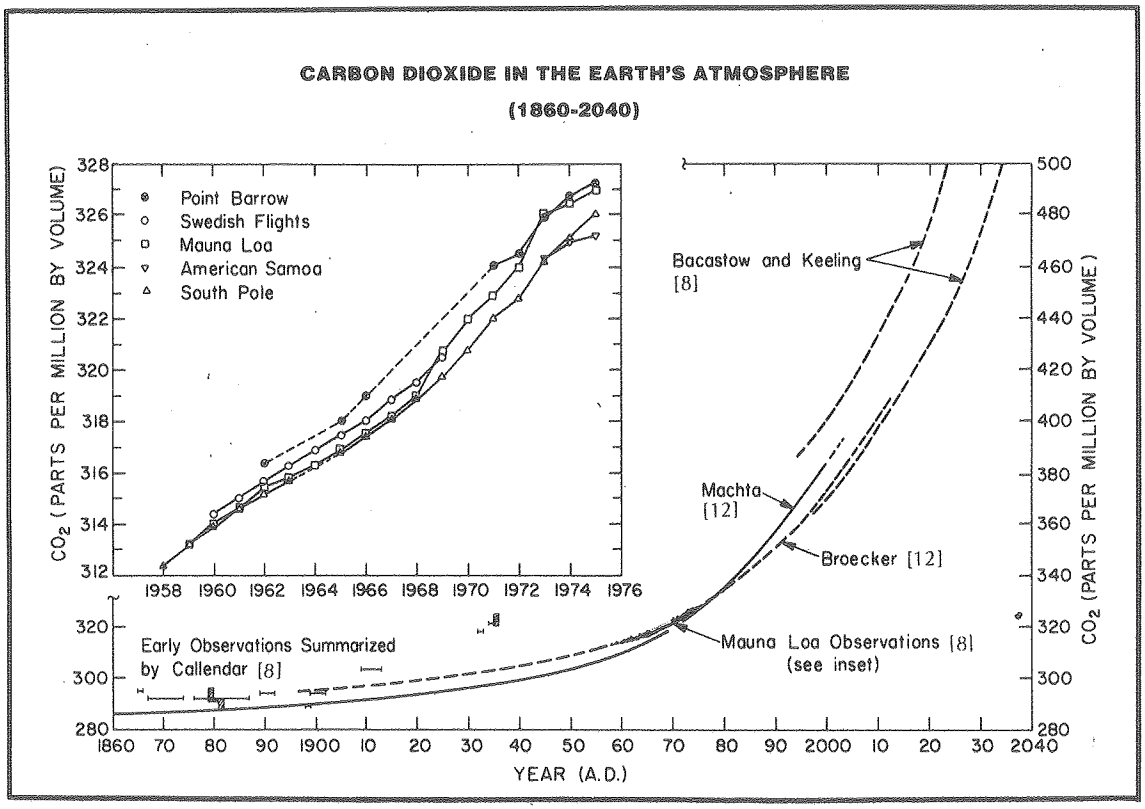
BaP - 10 lbs/day

	BaP concentration
PETROLEUM - - - - -	1-5 ppm
COAL OIL - - - - -	10-100 ppm

XBL 773-4287

worldwide as well. The amount of benzo(a)pyrene (BaP) in the oil produced from coal is shown in the bottom of the picture to be of the order of 10 to 100 parts per million, whereas the amount of BaP in natural petroleum is only 1/10 or 1/20 as much. This problem is not an insurmountable one: that BaP can be removed from the oil, i.e. the oil can be cleaned and purified of the BaP so that when the oil is burned there will be considerably less BaP in the exhaust from such oil. There will be a cost for doing this, but the environmental requirement for it will be so great that it will have to be removed. This is really a soluble problem, a problem for which we can invent or devise a solution which can be implemented.

The second principal constraint on the expanded use of coal is the fact that when one burns coal (or any other fossil carbon, for that matter, but coal in particular because it is the highest producer) carbon dioxide must be produced. The rate at which carbon dioxide is being produced upon the surface of the earth is higher than the rate at which it is being removed by the green plants and by the oceans, as shown in Figure 4. Here, in the upper lefthand corner, you see an inset which shows the rise of CO_2 from 1958 to 1976 measured at five different stations across the globe: Point Barrow in Alaska, one at the South Pole, one on Mauna Loa in the Hawaiian Islands, one on American Samoa, and one over Sweden. All of these sites indicate the same result: a rise in CO_2 from 310 parts/million to about 330 parts/million in the last 15 years, or roughly a 5% rise in 15 years. By measuring the isotopic composition of the wood in the rings of ancient trees, we can estimate the level of carbon a hundred years ago. The major curve in this figure shows what has happened in the last century, from 1860 to about 1980: the rise has been about 15%, from 290 parts/million to 330 parts/million. The projections here represent a number of possible consequences, depending upon the different



W.W. Kellogg
Bull.Atom.Scien., Feb. 1978

XBL 783 - 3858

rates at which fossil carbon, in the form of coal, is used. The four alternatives shown would all produce a very large rise in the expected CO_2 level by the year 2020 or thereabouts. There is no escape from this if we continue to burn fossil carbon from underground--particularly coal, since it produces more CO_2 per unit of heat or energy.

What are the possible consequences of this rise in the CO_2 level? It is known that CO_2 is transparent to the visible light from the sun, as shown in Figure 5. The visible light comes right in through the carbon dioxide blanket. However, when the sunlight strikes the surface of the earth at any point, whether it be in the green plant, on a brown rock, or the ocean, it will eventually be converted to heat. Then an attempt will be made by the earth to reradiate that heat, but when that happens, the CO_2 will not permit the heat or the infrared to escape from the earth's surface--it will reflect it back. Therefore, the surface of the earth will become warmer and, as a result of that, the entire climatic pattern of the earth's surface can be expected to change: the rainfall patterns will be different, and the places in which people can grow food and live will be very different from what they are today. And so it behooves us to find other ways to supply the energy needs of mankind without burning the fossilized photosynthetic product which is now stored in the ground in the form of coal.

The only convenient way that we have of doing this, without producing a net increase in CO_2 level and without producing other environmental hazards, is to use the natural vegetable productivity of the earth. The principal way in which sunshine is converted today into chemical energy for use as material or fuel is by the photosynthetic process of the green plant. The places on the earth's surface in which this happens is shown in Figure 6. Here you see that about one kilo of carbon is reduced per square meter per year. This is mostly in the equatorial parts of the earth (the Amazon, the Congo, and

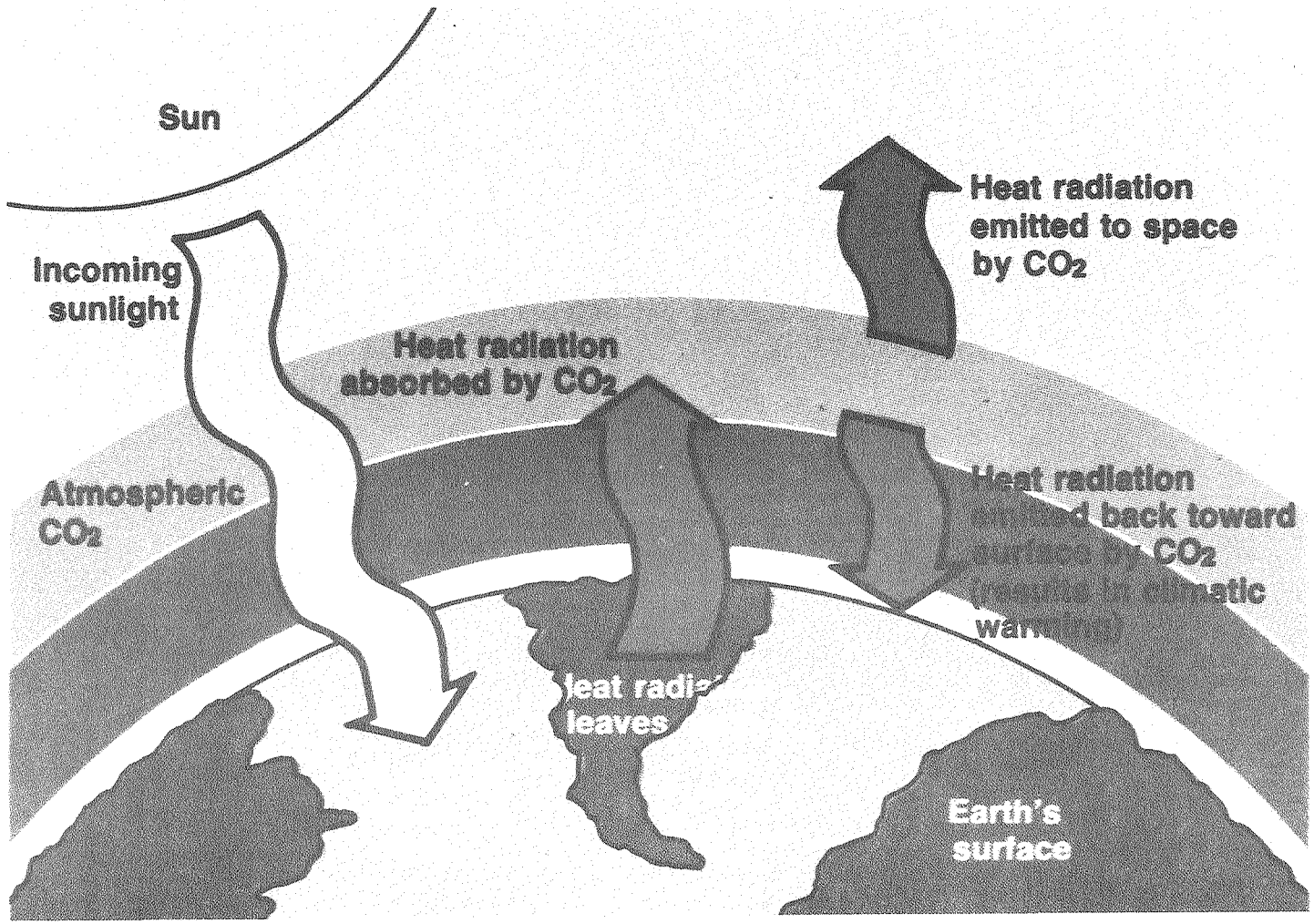


Figure 5. Greenhouse effect

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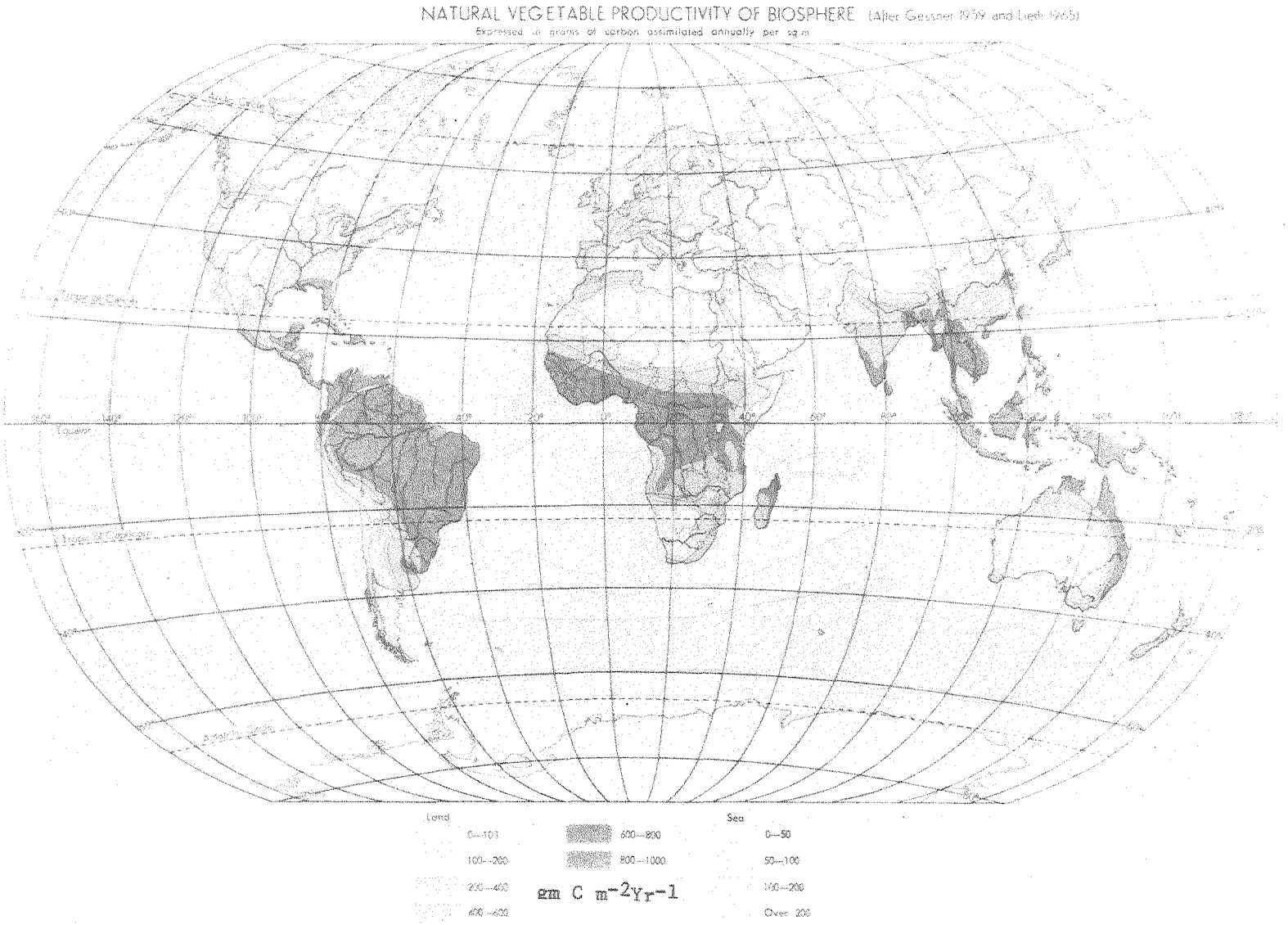


Figure 6. Natural vegetable productivity of the biosphere

CBB 741-129

Southeast Asia) where it is both humid, warm and sunny. These are the natural regions of highest vegetable productivity. We cannot cut the trees with impunity, but we can harvest their products. However, there are many regions of the earth which have a very high solar insolation but which are not very productive today in terms of vegetable productivity for the simple reason of lack of water (the South African desert of Kalahari, the Southwestern desert of the United States, a good part of the Northeastern desert of Brazil, etc.). It is in an attempt to use such regions that we are now engaged.

The first effort to do this has been very dramatically demonstrated, both in Brazil and in the United States, using a grass for this purpose. That grass in Brazil you know as sugar cane. In the United States we cannot grow sugar cane on the scale that is necessary, but we can grow corn, which is a very close relative of sugar cane. With both corn and sugar cane there is already a very substantial effort being made to use these products, insofar as they do not compete for food production, as a source of energy and materials. In Brazil, sugar cane is grown in much of the Northeastern part of the country. In Australia, of course, a very large amount of sugar cane is grown, again in the Northeastern section of that country. This sugar cane can be harvested not only for food but, as there is more of it than is needed for that purpose, it can be harvested also as an energy crop, and the fermentable sugars converted into the convenient fuel and chemical--ethanol. This is being done on a very large scale in Brazil. Presumably you expect to harvest enough cane within the next five years to produce 20 billion liters of alcohol in one year as a source of fuel for automobiles and also as a source of chemicals for the petrochemical industry.

Figure 7 is a photograph of a sugar cane field in Australia, showing the burning of the cane just prior to harvest. The ripened cane has very dry leaves, and it is not possible either for man or machine to enter into the crop until

CBB 770-11766

Figure 7. Sugar burn, Mackey, Australia

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2$$

180 gm (673 Kcal) — 92 gm (655 Kcal)

12.88 lbs ⟶ 1 gal. (84,356 B.T.U.)

Cost / gal. = raw material + ~20¢ process cost

XBL7411-8086

the dry leaves are burned away. This burning process looks exactly the same in Brazil and in Puerto Rico as it does in this photograph. This seems to me to be a tremendous waste of energy. We should invent a machine capable of harvesting all of the cane, instead of burning it off in this fashion.

After the cane is burned it is cut and crushed, and the fermentable sugar can then be converted into a more useful form--a liquid fuel or chemical, ethanol. This is done by a simple fermentation which here in Brazil is very highly developed, except for the alcohol-water separation step. I want to briefly show the stoichiometry of that fermentation to illustrate what happens to the material (Figure 8). Here you see the conversion of 180 grams of sugar into 92 grams of alcohol, i.e. a solid is converted into a liquid of half the weight, and the calories are conserved. There is practically no loss of energy in this conversion, so it is a very efficient fermentation conversion.

In the United States we cannot do this, because we do not have enough cane for this purpose. However, we do have enough corn--the corn that is being grown in Nebraska and all through the Midwest as a source of feed for cattle. If we could divert some fraction of that corn from cattle feed to alcohol fermentation and then use the distilled dried yeast which is a byproduct from the fermentation for cattle feed, I think it might be possible for us to use this corn not only as cattle feed but also as an alcohol source, without any major disruption of the cattle meat industry.

While most plants store their energy as carbohydrate, in the form of sugar or polymerized sugar (cellulose); some plants store their energy as fully reduced carbon, in the form of hydrocarbon. The commercial example of this, of course, is the Hevea rubber tree, which originally grew in Brazil as a commercial product. It produces a latex, which consists of approximately one-third hydrocarbon emulsion in water. Figure 9 shows a tapping of a Hevea rubber tree in Brazil. While it is true that the latex of the Hevea rubber

CBB 757-5366

Figure 9. Rubber tap, Brazil

tree is only 30% hydrocarbon, the value of that hydrocarbon is very high--because of its high molecular weight. Because it is more valuable as an elastomer (i.e., as a rubber) than it would be if we broke it down into smaller molecules to produce ethylene and polyethylene, we do not wish to destroy this high molecular weight of the Hevea. We must find other sources of hydrocarbon producing plants which do not make hydrocarbons of such high molecular weight.

We began this work about four years ago, with an analysis of many of the alternative sources of hydrocarbon which we had begun to collect from Brazil and elsewhere. We began the analysis of many of the hydrocarbon containing latexes which do not produce rubber, but which produce a hydrocarbon of lower molecular weight.

We wanted to use plants that would grow in the semiarid parts of the world which are not now productive of food crops. One of the things we knew, of course, was that there was a plant belonging to the Compositeae family (Hevea belongs to the Euphorbiaceae family), growing in the Northern desert of Mexico. Figure 10 shows one of these plants, called guayule, which is also found growing in the Southern United States, in Texas and in Arizona. However, the guayule produces a latex very similar in molecular weight distribution to Hevea, and hence useful as rubber. Therefore, we did not wish to use guayule as a possible source of hydrocarbon for oil.

In looking further, we began exploring other members of the family of Euphorbiaceae, to which Hevea belongs as one genus. We encountered another genus of Euphorbiaceae known as Euphorbia, which has about 2000 species. The Euphorbias grow in all kinds of climates, both wet and dry, and in all sorts of forms, small plants as well as trees. I would like to show you a few photographs of these Euphorbias from which we have collected latex, and which we have now analyzed.

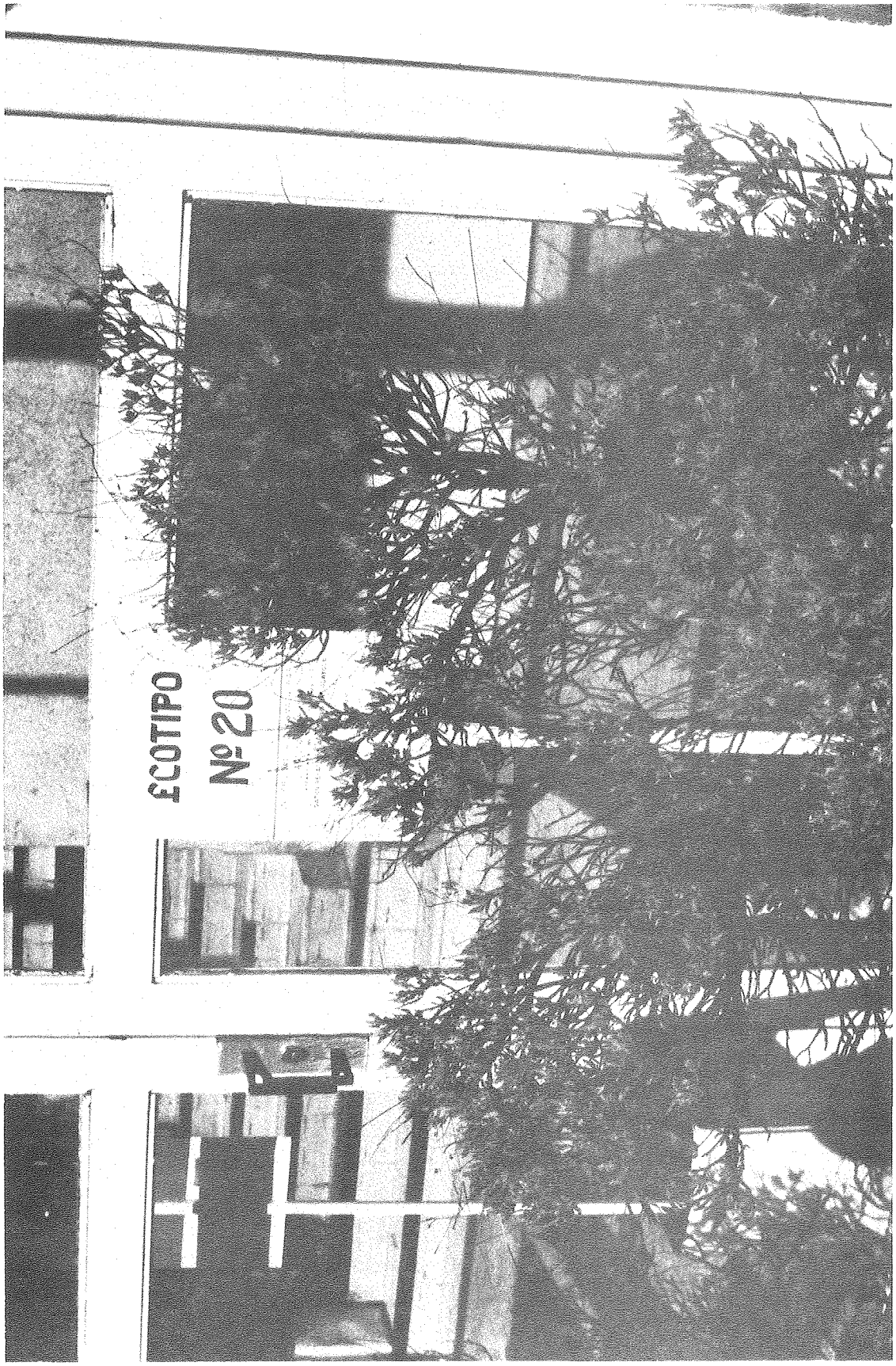


Figure 10. Guayule, Saltillo, Mexico

CBB 778-7592

Figure 11 shows a Euphorbia growing on the South Coast of Puerto Rico, and Figure 12 shows the flow of latex when it is tapped. This one is called the Euphorbia lactea or Euphorbia trigona, which are very close to one another but not quite the same. The E. trigona we first saw in Piracicaba, Brazil. We have collected some of that latex.

Figure 13 is a common one, Euphorbia tirucalli (known in Brazil as Aveloz), and is shown growing on a plantation in Southern California. It is about 20-30 cm high and about 30 cm in diameter. This is one year's growth, from the time we put it in the ground as a single 5 cm high cutting. Figure 14 shows a very large Euphorbia tirucalli tree, of unknown age, growing in Brazil. Figure 15 shows a Euphorbia tirucalli bush, about one year old, growing in Okinawa on a large plantation. I do not have the complete productivity data from Okinawa, but what I do have indicates that it is as productive as any of the Euphorbias that we have been growing in Southern California--perhaps even more so, because Okinawa is very wet, whereas Southern California is not.

I want to show you another Euphorbia, a completely different one, which grows wild in Southern California. Figure 16 shows Euphorbia dendroides growing on a hillside in Los Angeles. This is wild; it is not planted. They grow quite large--the whole hillside is covered with them. They are close relatives to the ones we have planted in Southern California and measured the growth rate of.

Figure 17 is a photograph of the latter plant, called Euphorbia lathyris. These plants are seven months old from seed, and have grown $1\frac{1}{2}$ meters in seven months. They are also growing in Okinawa, but the climate there is too wet for them to grow well; they grow much better in Southern California. Figure 18 shows the data that we have obtained on the growth rate of this plant in Southern California over the last ten months. These plants were germinated in the greenhouse in December, 1976 and were put in the ground in February, 1977. The dry

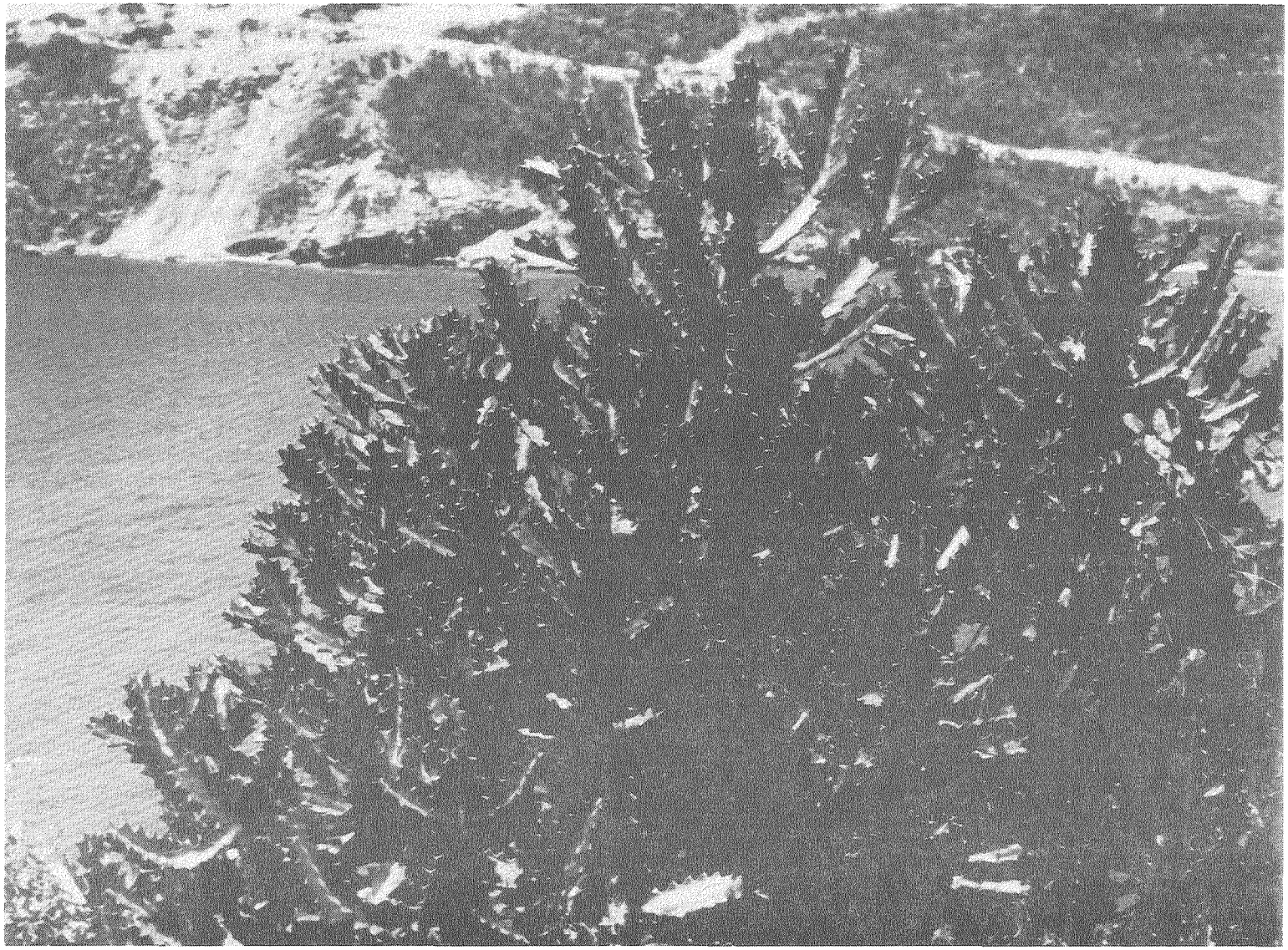


Figure 11. *Euphorbia lactea* tree, South coast of Puerto Rico CBB 775-5034

Figure 12. Euphorbia lactea tree, Puerto Rico, showing flow of latex CBB 778-7446

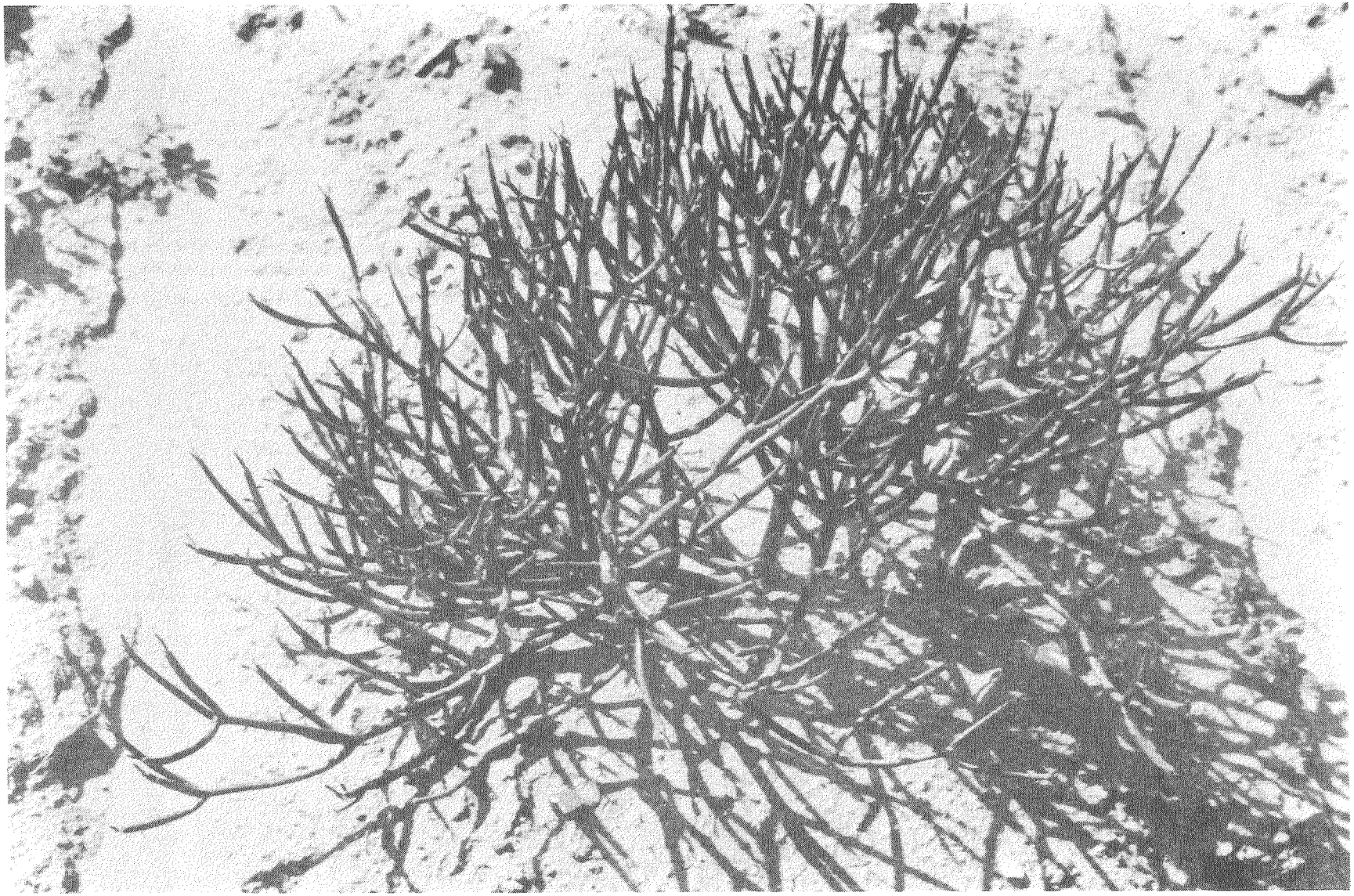


Figure 13. Euphorbia tirucalli, South Coast Field Station, Calif. CBB 785-6451

Figure 14. Euphorbia tirucalli, Brazil

CBB 768-7677

Figure 15. *Euphorbia tirucalli* bush, Okinawa, August 1977 CBB 779-8869

CBB 782-1095

Figure 16. Euphorbia dendroides, Los Angeles, California

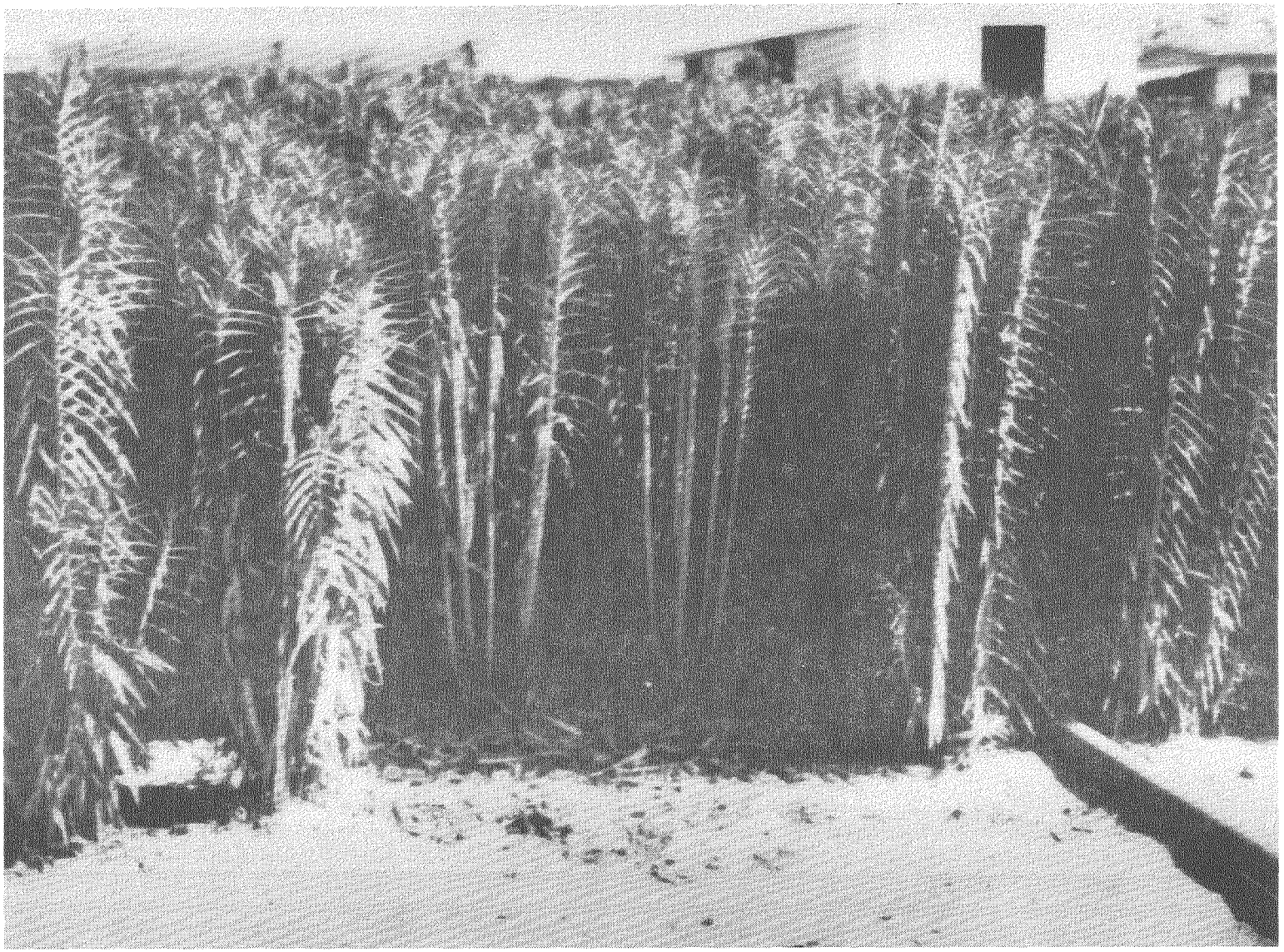
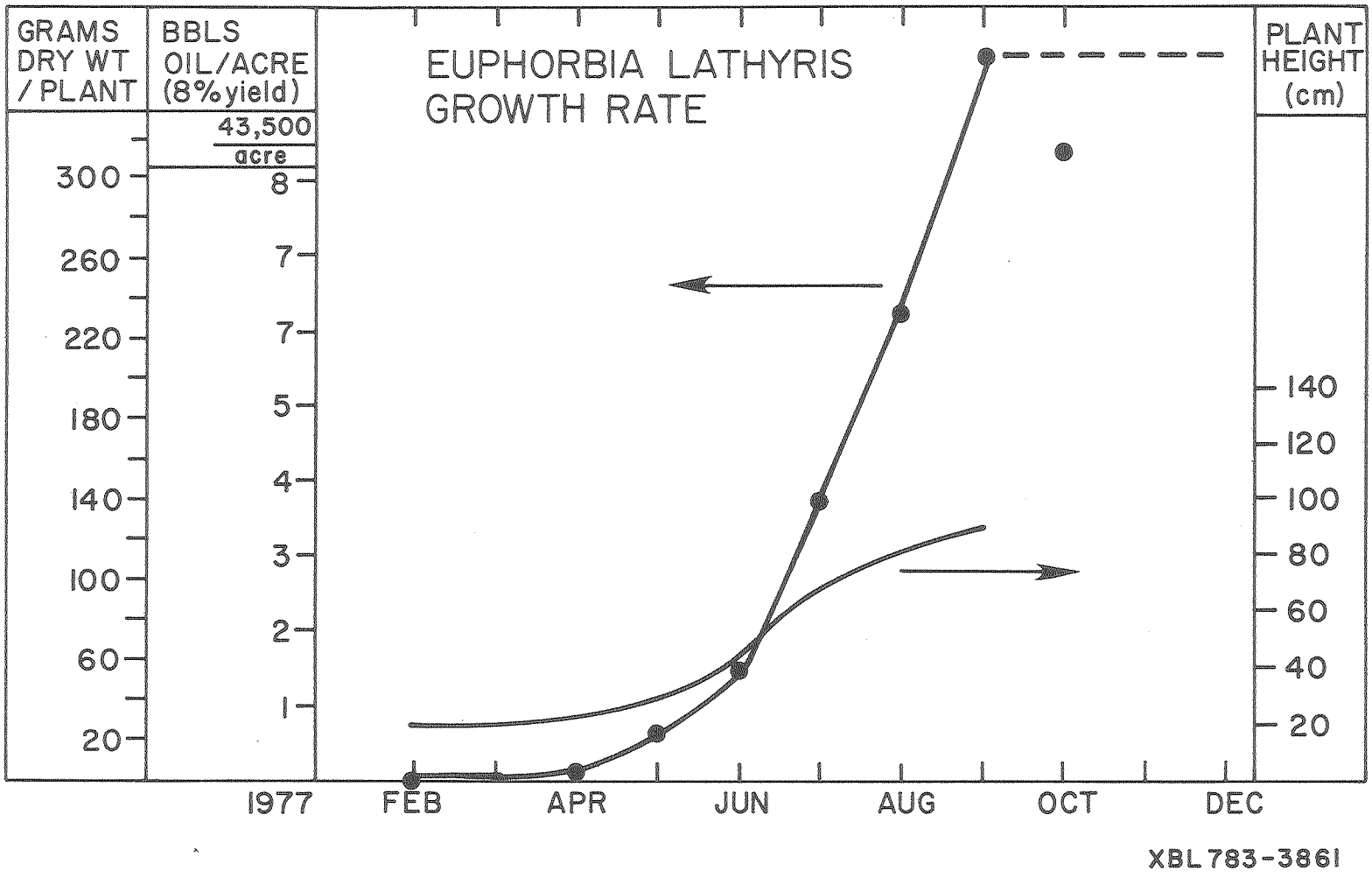


Figure 17. Euphorbia lathyris, South Coast Field Station, California CBB 779-9182


GRAMS DRY WT / PLANT
BBLS OIL/ACRE (8% yield)
43,500 / acre
EUPHORBIA LATHYRIS
GROWTH RATE
PLANT HEIGHT (cm)
300
260
220
180
140
100
60
20
8
7
7
5
4
3
2
1
140
120
100
80
60
40
20
1977
FEB
APR
JUN
AUG
OCT
DEC

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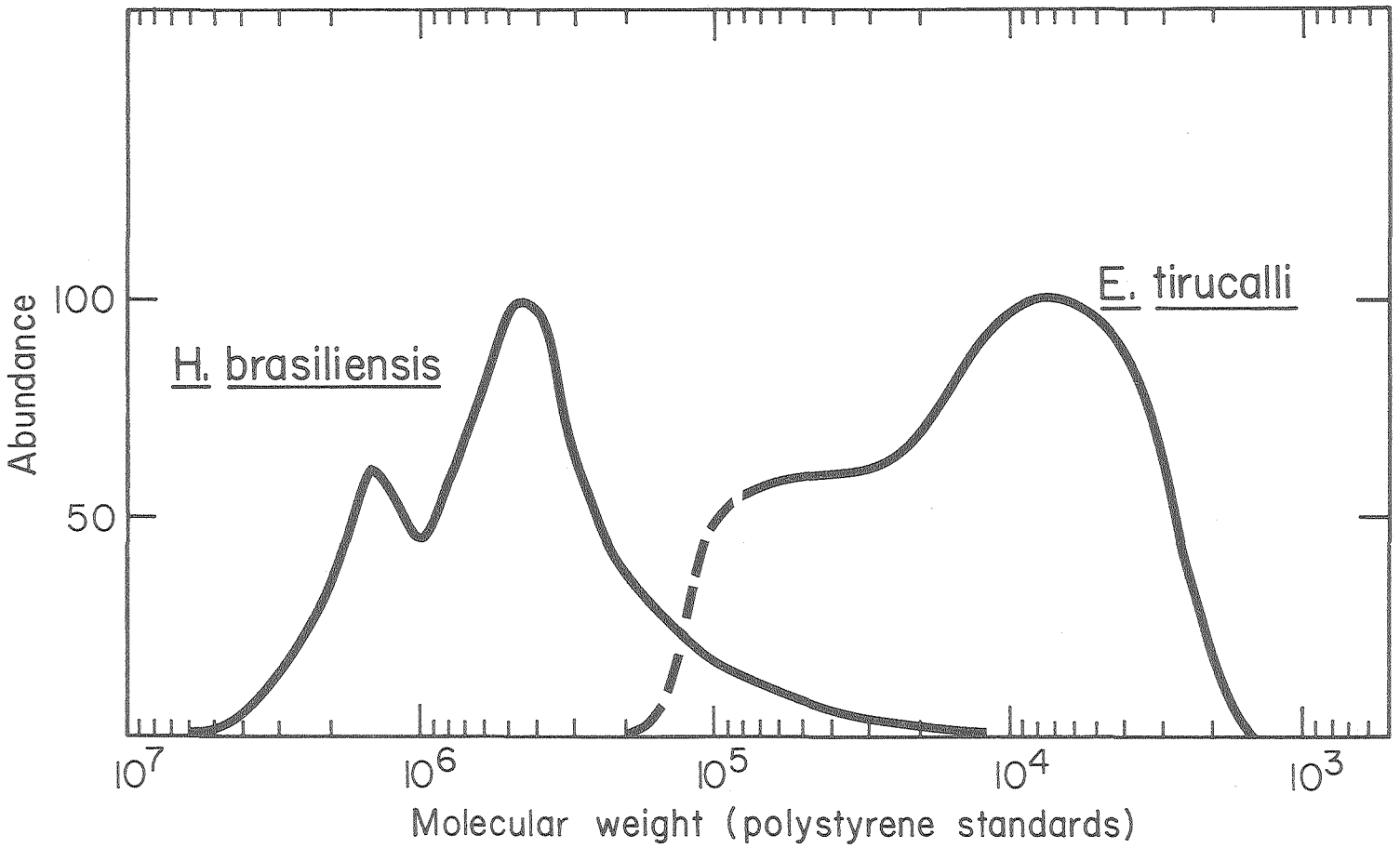
weight is shown on the far left of the graph. In October, 1977 it became too cold for them to continue growing, and they went into a 6-month dormant phase. They are now going to seed. We have analyzed these plants in the course of their growth. The Second column on the left side of Figure 16 shows you the conversion of their total oil content into barrels of oil/acre. To convert that figure into barrels of oil/hectare, you simply multiply by $2\frac{1}{2}$. For maximum oil content they could have been harvested in September, at which time they could yield 10 barrels of oil/acre in about nine months, or about 25 barrels of oil/hectare. This is a substantial production.

This oil is a mixture of hydrocarbons consisting mostly of terpenoid isoprenes--not only open chain isoprenes, but cyclic isoprenes: diterpenes and triterpenes, sterols, etc. We published an article in Science a few months ago, and we will publish more of this information in the near future about the various kinds of detailed materials that are present in that oil mixture.

I would like to show you the crude mixture molecular weight distribution of this oil compared to that of the hydrocarbon from Hevea. Figure 19 shows that Hevea has an average molecular weight of somewhere over a million. This happens to be a curve with bimodal distribution, half a million and two million, whereas the other curve, for Euphorbia tirucalli (the one that grows well in Okinawa and Brazil), has a very small molecular weight--about 10,000. So, the latter is a possible candidate as a crude oil mixture of many different terpenes as well as some open chain polyisoprenes.

Most of you are familiar with the biosynthetic sequence which will produce polyisoprenes. Let me just remind you of the last step. The first products of the plant are sugars, particularly phosphoglyceric acid. From there we can go to pyruvic acid, and from there to aceto-acetic acid. From this point we go, by reductions, to beta-hydroxy glutaric acid, and then to mevalonic acid. After pyrophosphorylation, reduction and decarboxylation, we get isopentenyl

Molecular weight distribution of polyisoprenes isolated from Hevea brasiliensis and Euphorbia tirucalli



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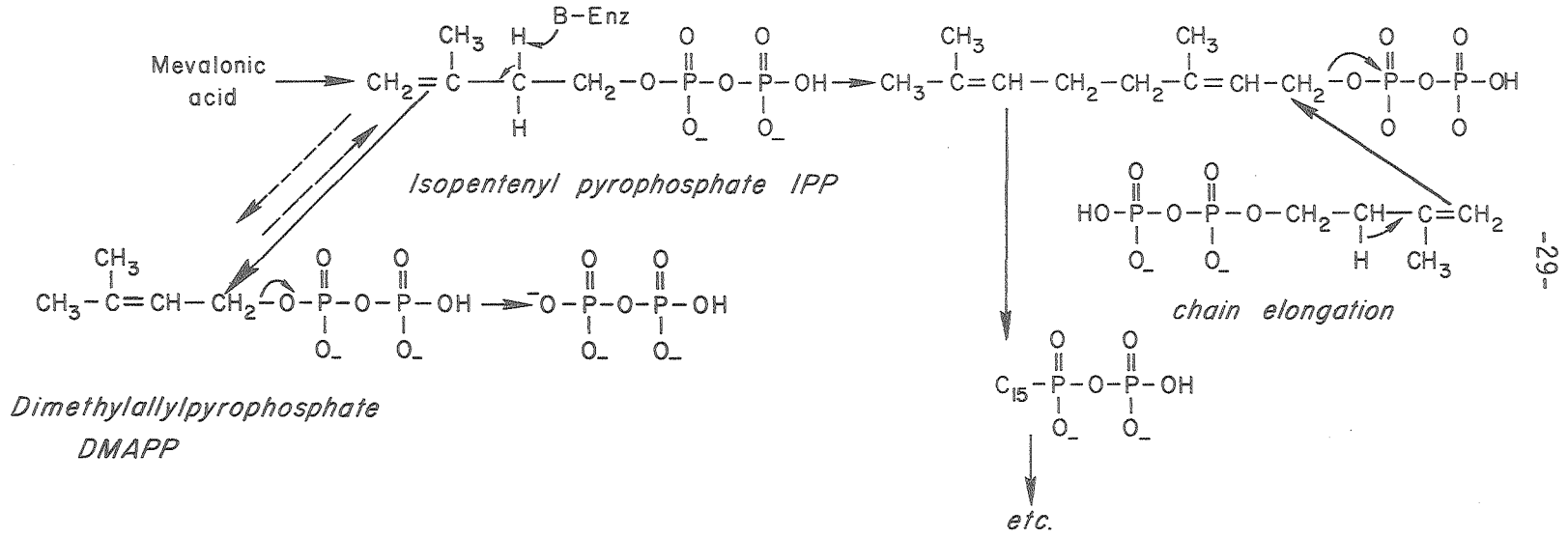
pyrophosphate, which is shown in Figure 20. From isopentenyl pyrophosphate, a five-carbon compound, we can isomerize part of it to dimethylallyl pyrophosphate. Then these two condense to form a C_{10} pyrophosphate which regenerates incipient allylic carbonium of DMAPP which can then continue to grow on another isopentenyl pyrophosphate, so that the chain elongation can continue. I just show you this to remind you of the sequence from sugar through glyceric acid, pyruvate and aceto-acetate, beta-hydroxy glutarate to mevalonic acid and isopentenyl pyrophosphate. It is a sequence which you all know, and this is the terminal step in that synthesis.

Now I stated that we could grow about ten barrels of oil (mixed hydrocarbon) per acre in nine months, and this is accompanied by about 15 tons of dry lignocellulose. The cost of growing such a crop in the parts of the United States which today are non-productive of food crops (Texas, Arizona, Southern California and Southern Florida) is about $100.00 per acre. This is with wild plants that have not been improved, and in which there has been no selection. With these wild plants, we are getting ten barrels of oil per acre, which costs about $100.00 per acre to grow--so the cost of growing the oil in the United States is about $10.00 per barrel per acre.

I have discussed with my friends in Chemical Engineering and Agricultural Engineering how much it would cost to cut the plant, to crush it, and to extract the oil. We do not yet have a commercial process for this. Using the laboratory process, which is a very ordinary kind of chemistry using solvent extraction, and which probably could not be done on a very large scale (involving millions of barrels of oil), the cost would be about $10.00 a barrel to take it from the plant and to put it in the barrel. Thus, we would have oil in the United States for a total cost of $20.00 a barrel--$10.00 a barrel to grow it, and another $10.00 a barrel to put it in the barrel--without improvements, either in growing or in processing.


Mevalonic acid
B-Enz
Isopentenyl pyrophosphate IPP
Dimethylallylpyrophosphate
DMAPP
chain elongation
etc.

XBL 771-4113

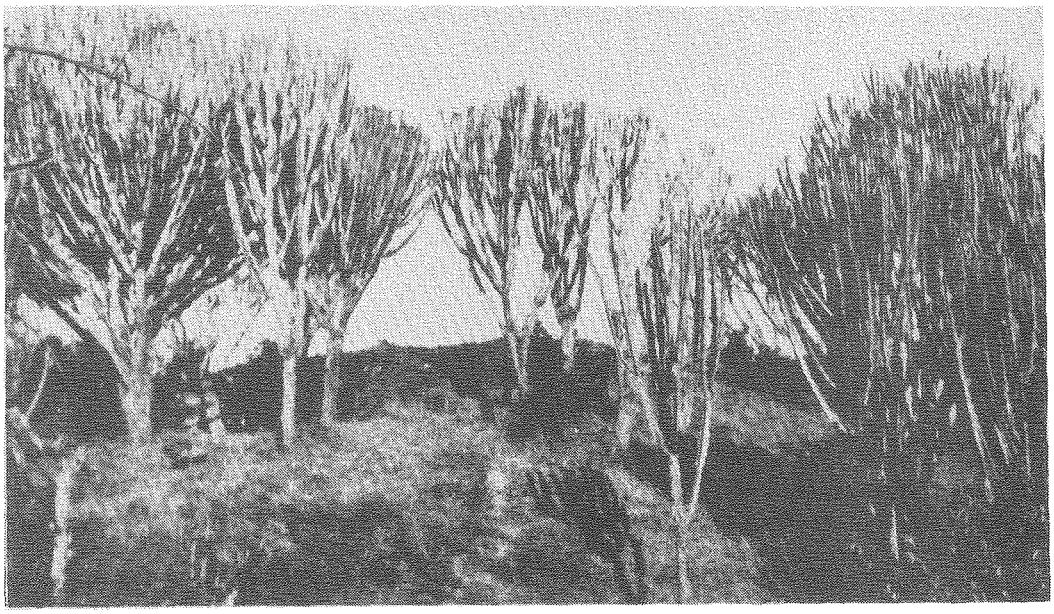
If this can be done, and if I can persuade some of the oil and the chemical companies in the United States to try it, then we will not have to spend the dollars in Arabia--we will be able to spend our money inside the United States. If the Brazilians can do it (and I expect that they will, because I know that already one company, and maybe two, are growing these materials in Brazil), then the whole picture would change.

I think we are already on the edge of economic viability with these plants, even just treating the material as crude oil, not as a chemical. In addition, this mixture of hydrocarbons will have in it many different sterold, many different diterpenes and diterpenols, some with very interesting biological activity which could be developed. The total value of this product as a new raw material will become even greater than it is today. Today it is still a "wild" plant (or a whole group of "wild" plants), not yet "domesticated", not yet an agricultural staple or crop.

As agricultural chemists, you can see that this crude mixture of hydrocarbons and hydrocarbon alcohols will have in it many things of higher value than simply a fuel or raw material for cracking in a petrochemical factory. With genetic and agronomic improvements, I expect that the yield will go as high as 20 or even 30 barrels per acre. Even with only the proper selection of plants, it will rise. When we get to the 10 or 20 acre size for our plantation, we will be able to develop a good commercial extraction process--one which would not use organic solvents, only water, followed by a catalytic reformation of the whole water extract. The prices will go down--I am sure you need no persuasion of that.

In passing, it should be noted that this very idea was broached by the Italians in Abyssinia, back in 1938, as shown in Figure 21.

I would like to say in conclusion that ultimately, in the last analysis, we must be able to reproduce the quantum (or light) capturing system of the



Forest of *Euphorbia abyssinica* var. *eritea*. Photo by Prof. Baldrati, Asmara, Eritrea

A New Brand of Gasoline

One of the major problems in Italy's recently conquered province of Ethiopia is fuel for motor cars. The need for gasoline is urgent as almost all transportation is dependent upon motor cars and because all motor fuels have to be imported at extremely high prices. During the subjugation of 1935, an oil company entered into a contract with Haile Selassie for all oil rights in that country. This gave the Italians wild expectations of an unlimited supply of crude oil, but these dreams have not materialized, ardent though the search has been.

Alcohol, the substitute for gasoline, can be made from palm nuts, corn and millet which are available in sufficient quantities to produce an estimated one million gallons per year, but petroleum is best and most desirable as a motor fuel and so far the country has produced none.

By this time the reader will perhaps be wondering what all this has to do with succulents, but the unusual association is that the Italian Fuel Commission announces that the best assurance now appears to be in the billions of weird cactoid Euphorbias that grow throughout that country. The latex of the large tree-like species is said to yield approximately 60% of a gasoline-like liquid which can be produced by a simple chemical treatment at little expense, and today this "vegetable gasoline" holds out an encouraging hope to the worried Italian engineers. The Italian Fuel Commission is at least going to try it out and are now arranging for the construction of a Euphorbia gasoline refinery at Agodat, which is the center of the large Euphorbia forests and on the main highway to Adis Ababa where fuel-hungry fleets of trucks pass every day on their trips to the sea.

The entire experiment will be watched with interest since geologists inform us that the worlds petroleum supply is limited and deminishing rapidly, and who knows but that the answer rests with the Euphorbiae.

G. A. FRICK

Figure 21.
Article by G. A. Frick, Cactus & Succulent J. 10, 60 (1938)

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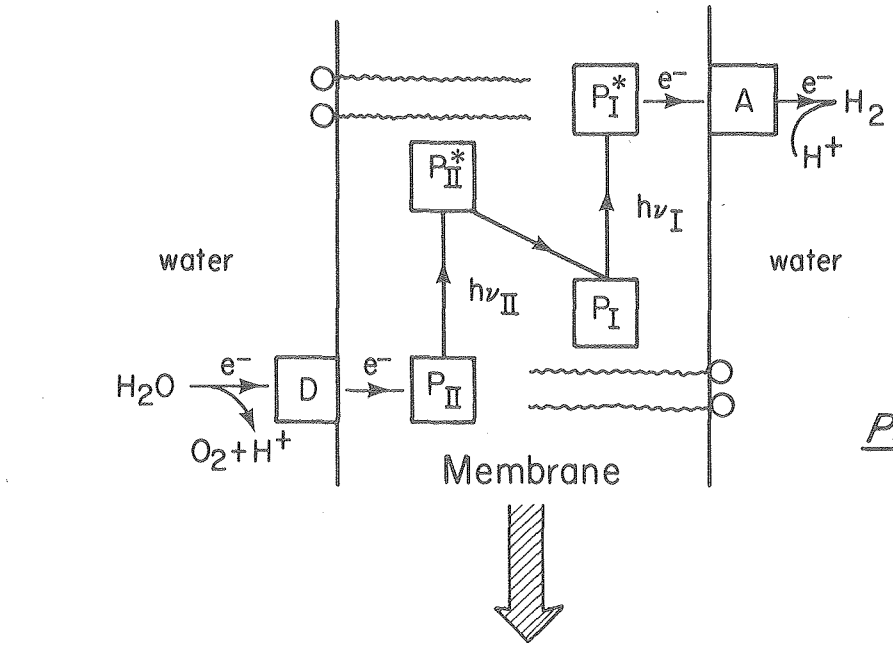
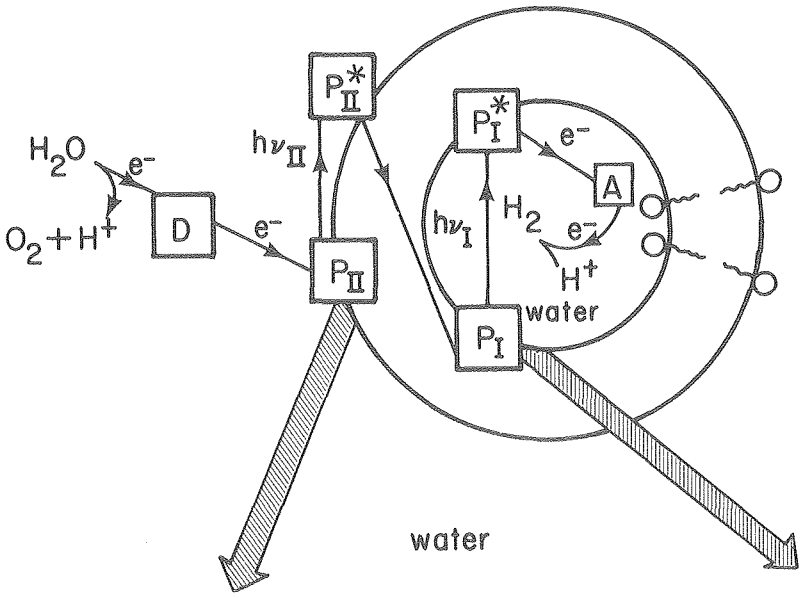
plant artificially. We should not have to grow plants in order to catch the sunshine. But in order to do that, we must understand how it is done by the plant. If we understand exactly how the plant does it, then we have a possibility of doing it without the plant--synthetically and artificially. We can make a system for catching the quanta or light from the sun and reducing organic carbon, or photolyzing water, to make a useful product. In fact, we have already taken one step in that direction, which I would like to show you. In Figures 22 and 23, you will see a model of a photosynthetic membrane in a green plant. It is a bilipid membrane, with two surfaces for the two quantum act: Photosystem I and Photosystem II (two different sensitizers). We cannot use chlorophyll, because it is not stable enough; so we have made many artificial surfactant dyestuffs. We have made the membrane in the form of a vesicle, and have put the dyestuffs on the inside and the outside surface. We have put a donor system inside and the acceptor outside, and have shown that we can photochemically transfer an electron from one side of that membrane to the other. What we cannot yet do is to generate molecular oxygen. That would require a manganese complex, and we do not yet know what that is; but we can make the hydrogen, using methylviologen and platinum. So the manganese complex is not yet known, and that is the big problem which remains to be solved before we can make a synthetic system work. I am sure that somebody will find out what it is and how to make it within the next decade or so. And thus we will be free of the need of arable land to capture the sunshine for energy and materials.

PHOTOELECTRON TRANSFER SCHEME



Photosynthetic Membrane



Vesicle

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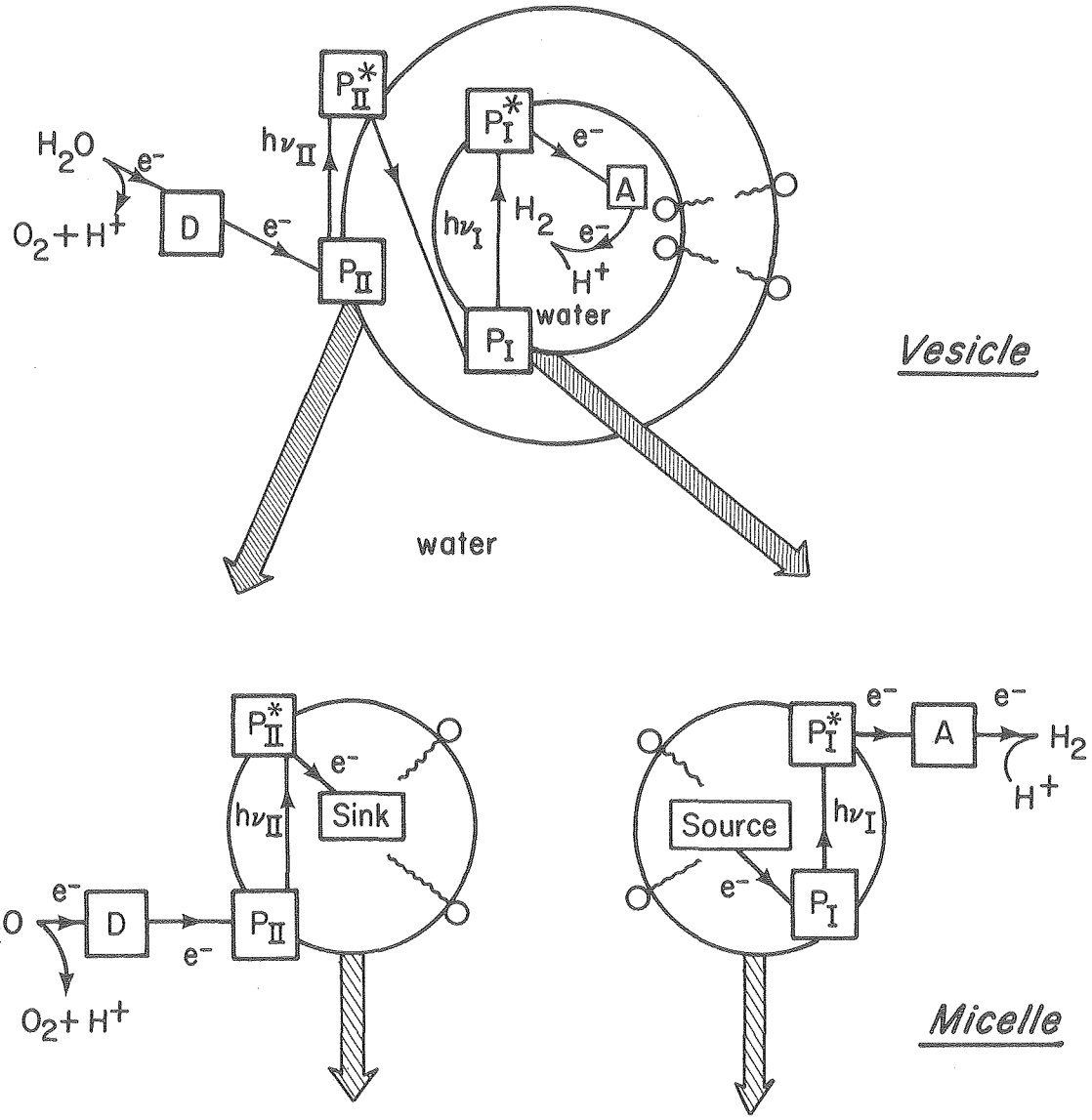
PHOTOELECTRON TRANSFER SCHEME



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