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ENERGY AGRICULTURE

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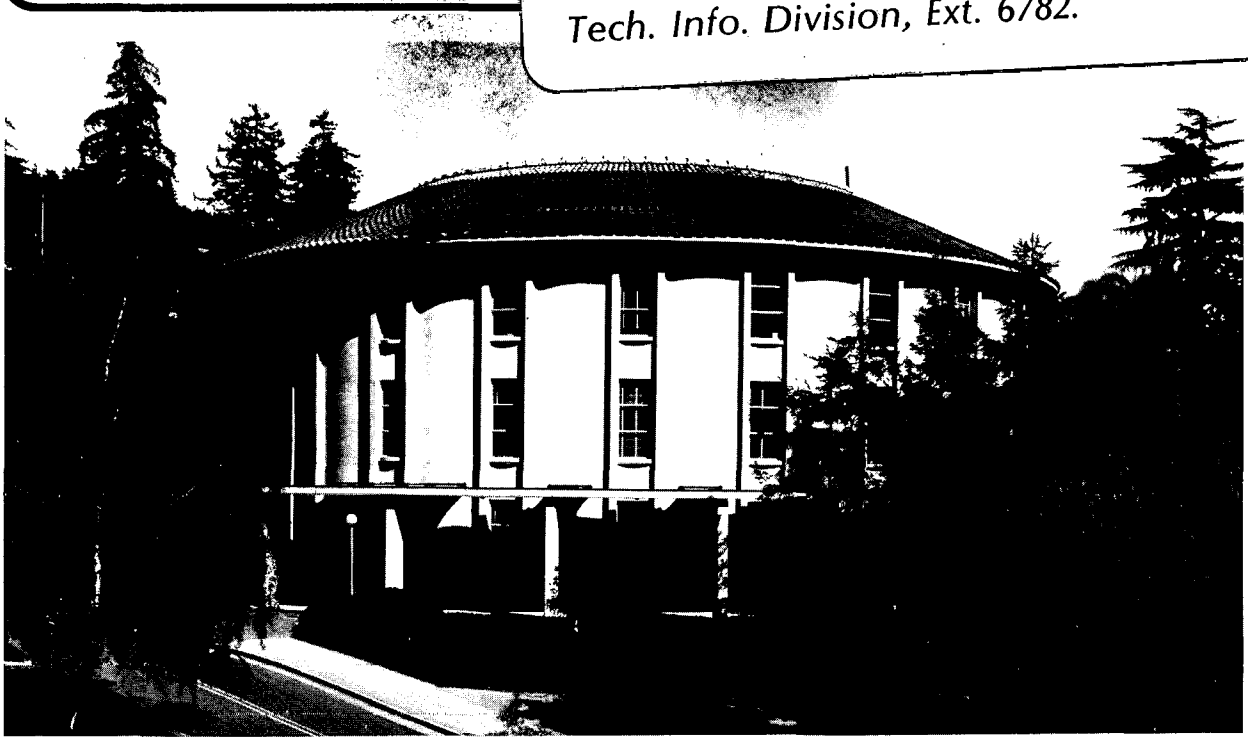

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# ENERGY AGRICULTURE

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## Abstract

That we will require renewable fuels for the future seems an almost obligatory need. This will be largely due not only to the exhaustion of our existing clean hydrocarbon (and possibly gas) reserves, which are the products of ancient photosynthesis, but also to the almost intractable air pollution problem which the combustion of fossil carbon to carbon dioxide produces. The most immediate source of renewable fuel is, of course, the annually growing plants themselves, some of which produce hydrocarbon directly. In the more distant future, the mechanisms by which the plant captures solar quanta and converts them into stable chemical form may be useful in devising totally synthetic devices which will perform a similar function.

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## INTRODUCTION

Why should we be concerned with renewable fuels for the future? The pattern of use in the United States for 1980 is given diagramatically in Fig. 1 and from that it is possible to find out what energy gains and costs might be for different types of activity. This figure contains three messages: One, on the left hand side, indicates that the origin of over 95% of our total basic energy sources are oil (33.8 units), gas (20.8 units) and coal (19.0 units), out of a total of 78 units. All three of these are the fossilized remains of ancient photosynthetic processes which took place in the green plants several hundred millions of years ago and the products of those plants were laid down in the ponds and oceans and converted into these three fossil forms of carbon. Secondly, on the right hand side, there is an indication of the total of the amount of energy put in at the left which is lost to some useful purpose at the right; i.e. the end use losses as waste heat in the conversion processes thru which we put the energy. The biggest percentage loss is in transportation. Out of the 18.6 units that go in, 16.4 are lost as waste heat; in the case of the automobile, for example, that heat is dissipated by the radiator into the atmosphere in order to generate the mechanical energy to run the wheels; 95% of the energy that goes into the automobile is acutally lost, and only a very small fraction is left for true work. This same type of thing is true for the airplane as well. In the center part of the chart we generate electricity, and conversion and transmission losses represent 18 out of the 25 units put in. The reason for this resides in a simple thermodynamic requirement. In both cases--electricity generation and transportation--we are converting the stored chemical energy first into heat and then using that heat to run mechanical

devices, i.e., converting the heat into mechanical energy. The Carnot limitation must be obeyed, that is, in order to convert heat into mechanical work the heat must flow from a higher temperature through the engine and be dissipated at a lower temperature; the heat flows from a high potential to a low potential. The heat flows from a high temperature through the engine to a low temperature, which is what makes the wheels turn. The heat must be discarded at the low temperature, and the efficiency of such a thermal engine is measured by the difference in temperature between which the heat flows: the higher the temperature at the input end and the lower the temperature at the output end, the more of that energy is converted into mechanical work. For practical purposes, that difference in temperature between which the heat flows is limited. The properties of the structural materials limit the high temperature and the low end of the scale is limited by the temperature of the sea or the air into which the heat must be discarded. This essentially puts an upper limit to the most efficient conversion of chemical energy through a heat engine into mechanical work of something of the order of 30-35%. The best we can do occurs in electricity generation in which it is possible to run the heat up as high as the turbine materials will stand and can cool as low as you can get the cold water to run over it, which is about 36% approximately.

With that idea in mind and remembering that most of our energy is in the form of fossilized photosynthesis, the most convenient form of that energy is actually liquid or gas. A little less than ten years ago we were put on the alert for oil supplies, and it turns out that today at least a little less than 50% of our oil requirements comes from domestic U.S. sources, and this source is going to continue to drop. These oil and gas supplies are getting more and more difficult to find. There are several

ways to measure how much oil there is available, i.e., actually estimate how much oil there is, and one way is to look at the price. But that contains two components (1) the true geological availability and (2) the social/political factors that determine whether geologically available oil is available to us. The price is not really a measure of availability. I sought some other way to measure that availability. One way is to measure the barrels of oil that you can find per foot of well drilled (Fig. 2) plotted as a function of time. The number of barrels of oil achieved per foot of well drilled has been dropping steadily since 1945. This says that the cost of finding the oil is constantly increasing. The effort could be expressed in terms of how many energy units are required to find a barrel of oil, i.e., energy costs for drilling and extracting the oil: how many Btus, or other energy units, does it cost to produce a barrel of oil.[1] Quite clearly when the cost of finding a barrel of oil in energy units reaches the energy content of the barrel of oil itself, or surpasses it as is predicted for the year 2000, the energy cost of finding the barrel of oil you find. If it costs 10 million Btu to find a barrel of oil and the barrel contains only 6 million Btu, you won't drill for it, even if it is there. Therefore, we have to find alternative sources, and there is no question but that will happen within the next 20 years. In fact, in some places it has already happened. That means we have not more than 20 years to find another way of fulfilling the need for liquid fuel: portable highly concentrated chemical fuel.

## THE CARBON DIOXIDE PROBLEM: RESULT OF INCREASED FOSSIL FUEL CONSUMPTION

Most of the limits I have spoken of are for liquid fuel. We have, of course, a very large supply of carbon in the form of coal. Fossil fuel to be sure, which is still accessible to us in this country, and there are

those who suggest that all we have to do is to learn the technology of converting that carbon (coal) into a more convenient form, such as liquid or gas. There is a cost in doing that, not merely a large dollar cost, but a cost in the production of carcinogenic materials from the coal and, what perhaps is even more significant, an effect on climatic parameters which could result in overall change throughout the world. You may remember that about 20 years ago we were admonished to transform our stationary power plants from the unsafe and dirty fuel, coal, to a safer cleaner source, such as low sulfer oil and gas, which we did. Most of our power plants were converted. Now it is suggested that we return to coal again. The very reasons that we left coal in the first place are still with us, namely, acid rain having its origin in the industrial areas of the United States, the carcinogens which are emitted from coal burning power plants (polycyclic aromatic hydrocarbons which are well established carcinogens), and, of course, the solid ash. All three of those who can be eliminated from the stacks at a dollar cost. However, there is one effect which is irreversible if coal is burned, no matter which way the coal is burned (as solid coal in the boilers, or liquid coal, or gaseous coal), the act of getting the energy from the coal necessitates the conversion of the carbon of coal into carbon dioxide, and there is no way to avoid that if you get the energy out of the coal. The energy is the conversion of carbon with oxygen from the atmosphere into $CO_2$. This happens, of course, when you burn oil as well but the difference is that when you burn oil for every one atom of carbon burned, you burn two atoms of hydrogen. When you are burning coal, for every one atom of carbon you burn less than one atom of hydrogen. That means that for every energy unit that is generated when coal is burned, almost twice as many tons of $CO_2$ are generated as when oil is burned.

In recent years, in the last 20-30 years, we have burned relatively little coal compared to the oil. Nevertheless, the $CO_2$ level in the atmosphere has been rising continuously (Fig. 3). The $CO_2$ level rises in the winter and falls in the summer, but it never falls back all the way each summer. There is not enough green vegetation on the surface of the earth to take it all up, and the ocean doesn't dissolve it fast enough. The result is that every year we are left with a little more $CO_2$ in the atmosphere than we had the year before. In fact, the $CO_2$ level is rising faster now than it was 15 years ago. We can actually go back with our data to the 19th century by measuring the carbon-14 content of tree rings that were laid down at that time. Carbon-14 is generated by cosmic rays acting on the nitrogen of the atmosphere and so the carbon-14 level in ordinary $CO_2$ is determined solely by the cosmic radiation and the amount of nitrogen in the atmosphere. The specific activity of $^{14}C$ is determined by the total amount of carbon dioxide present, that is, the amount of $^{14}CO_2$ per million total $CO_2$ molecules is determined by the rate of formation and the total $CO_2$ that is already present. If we suddenly dump in nonradioactive carbon from coal (carbon buried in the earth for hundreds of millions of years, which does not contain carbon-14) into the atmosphere the number of carbon-14 atoms per million carbon atoms in the atmosphere falls, because we are injecting nonradioactive carbon into the atmosphere by burning coal which has no carbon-14. The amount of $C^{14}$ that is made remains constant, so the specified activity (concentration) of radioactive carbon falls. By measuring the carbon-14 concentration in the tree rings it is possible to find out what the $CO_2$ level was a hundred years ago. We find that the $CO_2$ level in 1880 instead of being 330 ppm, which it is now, was 290 ppm. In one hundred years the concentration of $CO_2$ in the atmosphere has risen

about 15%, but note now that half of that rise has occurred in the last 20 years. The concentration is rising more rapidly now than it did the first 80 years. We are burning much more fossil carbon today than we did 100 years ago, we are burning so much more oil now than we did in 1880 that the rate of dilution is greater today than it was then.

If we go back to burning coal (either directly or by converting it to liquid, gas, etc.) as has been suggested on the scale that we are now generating Btu from petroleum or natural gas, you can be confident that the $CO_2$ concentration would increase even more rapidly. The rate of rise would be approximately doubled in the next 20 years if we convert most of our energy needs from oil and gas to coal. Why should this make a difference? The answer lies in the physical properties of $CO_2$, which is a colorless gas, transparent to visible light, that is, the sunshine can come right through it. The visible light comes down to the earth's surface, and on the earth's surface ultimately all of the light is converted into heat. That heat is reradiated out from the earth. Therein lies the difficulty. As the heat tries to escape through the atmosphere there is the blanket of $CO_2$ through which the sunshine came as visible light, but the heat cannot leave as infrared light. The $CO_2$ absorbs the infrared and reflects it back down to the earth's surface again. It is as though you have a one way valve letting the energy in, but not letting it back out again. In other words, it is a blanket that warms up the earth's surface. The consequence of the $CO_2$, barring any other effects, is an increase in the earth's temperature and the consequences of that warming could be very severe.

Already there has been an increase in the $CO_2$ concentration in the last 100 years, and we can see a consequence of that rise in $CO_2$ which would lead to a corresponding rise in temperature? Are there any early warning

signs, can we see them, can we measure the increase in temperature which that 15% increase in $CO_2$ might have been expected to produce? Part of the trouble is that 15% change in $CO_2$ concentration would result, by almost any meterological model, in only a very small change in the average temperature of the earth's surface. The numbers that have been estimated for a global average temperature rise is somewhere in the 2-3 degrees range, which is almost within the noise of the measurement, and so it is very difficult to know whether we have already detected that rise.[2,3] There have been two other early warnings that have been found. One, is a decrease in the Antartic ice, which has been measured by various naval research vessels of the United States, Soviet Union and Great Britain. The consequence of the melting of a substantial piece of the South polar icecap would be a rise in sea level. Here, again, just in the last few weeks, a paper was published in which the sea level changes over the last 100 years have been recorded and it has been claimed that the sea level rise over the period 1980-1950 has been about 1 mm per year and that from 1950-1980 the rise has been roughly twice that, 2 mm per year, suggesting that here is another early warning measurement of the warming effect of the $CO_2$.[4]

Another consequence of the melting of the South Polar icecap which is sitting on one end of the rotational axis of the earth. If that ice is melted, the moment of inertia of that South Polar icecap with respect to rotation of the earth is quite small, and if that material from the icecap is distributed out to the seas, to the equator for example, the moment of inertia of that same mass will be larger, and that should slow down the rate of rotation of the earth, a quantity that can be measured to a high degree of accuracy.

We have now three quite separate early warning signals that the $CO_2$ effect is there. The fact of this increase, an experimentally observable global increase is unambiguous, and the consequences require an increasing global temperature. The microclimates at various parts of the earth are going to change, areas which have been suitable for agriculture will become unsuitable, areas which are unsuitable for agriculture today, say nearer the north and south poles, will become suitable, and I doubt very much whether the human race can adjust to such macroscopic changes in agricultural production even in two generations. This could be a very serious problem, and I think there are only two ways to avoid it, and one is not to burn coal especially, or even oil shale, and the other one is to catch all the $CO_2$ that comes out of the industrial/utility stacks, which may be a hopeless task, make dry ice out of it and drop it into the oceans, where it won't return because there is more calcium in the ocean bottom and also solid $CO_2$ is heavier than water. Down at the bottom of the ocean, the pressure is so high that it will keep the carbon dioxide down there, so it won't vaporize. To take all of the $CO_2$ out of the stacks of power plants, convert it to dry ice and drop it in the ocean would be a stupendous task technically and very, very expensive, of the order of $300/barrel oil equivalent. At that price, we can grow oil in green plants.

HYDROCARBONS FROM PLANTS AND TREES

How can we grow oil? Let me remind you that all fossil energy was originally made by the green plant cells of 300 million years ago by photosynthetic processes. The plants (green parts of the plants) caught the quanta from the sun, took the $CO_2$ out of the atmosphere, and with water, made sugars, proteins, hydrocarbons and other products, which were deposited, covered with mud and gradually formed such things as petroleum. We must now learn how to

harvest that reduced carbon that is produced annually by green plants. To do this we need to choose plants that reduce the $CO_2$ all the way to hydrocarbon,[5] rather than stopping at carbohydrate. The second alternative is to learn how the plants perform photosynthesis, and then mimic the green plant photosynthetic process and build a "machine" (device) that will do this; in other words, splitting the water molecule into hydrogen and oxygen.

We realized when we began this work that most plants store the sunshine not as oil, not as hydrocarbons, not as a chemical made up of only two kinds of atoms (carbon and hydrogen), but most plants store that energy as carbohydrate, i.e., carbon bound to one hydrogen atom and one oxygen atom. Some plants do store their energy in the form of hydrocarbons and the rubber tree is the best example. The original site of the rubber tree (Hevea brasiliensis) was in Brazil. Seeds were taken over one hundred years ago from the Amazon to the Kew Gardens in London, from whence seedlings were sent to Malaysia, the original "home" of rubber plantations. Our first effort was to visit Brazil to see if there were plants there, other than Hevea, which might be useful for hydrocarbon-production, i.e., for oil production. Rubber, of course, is essentially the same material (carbon and hydrogen) as oil, but has a much longer molecular chain. (We have learned in modern times to rearrange the atoms of oil to make synthetic rubber, and, presumably the reverse could be done, but that would be very wasteful. Rubber is worth 50¢/lb and oil is worth 5¢/lb, so the economics are obvious). If we could find plants that would make oil directly and grow on a more broadly based climate than the rubber trees, that would be a very useful thing.

That's why we went to Brazil about 8 years ago, where we collected soil samples and examined many different plant species in the Amazon region. The most interesting thing was that we found many other plants belonging

to the same family as the Hevea, the family Euphorbiaeceae, but we found that the Brazilians were growing enormous amounts of sugar cane, and producing from the molasses, left over after the crystalline sugar was extracted, alcohol by fermentation. The Brazilians were, even in 1974, considering using that alcohol, a liquid fuel, as an additive for their gasoline engines and as a replacement for hydrocarbons. We realized, as we went through the sugar mills, that they were wasting a certain amount of their cane productivity by harvesting for sucrose instead of harvesting it for fermentable carbohydrate. If the Brazilians were to do the latter, they could increase their fermentable sugar production by 10-15%, this has since occurred. In 1975 the decision was made by the Brazilian government to go into the proalcohol program, that is, make alcohol directly from sugar juice and use it as fuel for machines. In 1974 the production of alcohol from sugar cane in Brazil was 400 million liters, and by 1981 it was 4 billion liters. The Brazilians accomplished this by changing their harvesting procedures for sugar cane and also by building autonomous alcohol distilleries which were not part of the sugar industry at all. The Brazilians are using the sugar juice alcohol mixed with gasoline in their automobiles and as a 95% alcohol as a chemical feedstock.

EUPHORBIA LATHYRIS

There were many members of the family Euphorbiaeceae, such as the genus Euphorbia, which has many species, about 2000, which can grow in almost every climate, so we focused on Euphorbias. They will grow as small plants or large trees. Very early, we focused on the one that Mrs. Calvin had in the garden for quite another reason; because it turns out that this plant, Euphorbia lathyris, is known as the "gopher plant" and is used for pest control. This one is easy to grow and is the one that was used in

our experimental plantings at the University for the acquisition of agronomic data as well as the development of processing information and analytical data. The petroleum plantation at U.C. Davis is shown in Fig. 4. The plants are harvested by cutting, and are dried in the field; after drying the entire plant is extracted with hexane, the hexane is evaporated using steam generated by burning the residues. The processing sequence to recover terpenoids and sugars from Euphorbia lathyris has been developed (Fig. 5), with the result that from 1000 dry tons of plant material it is possible to get a yield of 8 tons of oil, and after the oil is removed, another extraction is performed and there is a further 200 tons of sugar. Keep in mind when you ferment sugar to alcohol, you get about one-half its weight in the form of alcohol with very little energy loss. The energy in the 200 tons of sugar can be harvested as 100 tons of alcohol, which is almost as much as the oil originally extracted. The major products, then, are 8 tons of oil and 100 tons of alcohol from 1000 dry tons of E. lathyris. What is left over is the lignocellulose (bagasse) which is used to recover the solvent from the extraction process, and there is still about 200 tons of excess bagasse which can be used to distill or purify the alcohol. The whole process is self-contained, the only gross energy input being the sunshine which is needed to grow the 1000 dry tons, on about 20,000 acres. This comes out to be roughly 6 barrels of oil/acre/year and 6 barrels of alcohol/acre/year, and that is using plants that have not been genetically selected or improved in any way. With that kind of starting material you can be sure that a few years of plant selection can easily double the yield.[6, 7]

When the oil from plants such as Euphorbia lathyris is subjected to catalytic cracking procedures it produces the usual suite of materials, very desirable ones indeed (Fig. 6), which are made today by cracking the

naptha distillate of crude oil: ethylene, propylene, toluene, xylene, nonaromatics, small alkanes and fuel oil.[8] The only "waste" product is 5% coke, and, therefore, it appears the 95% of the oil from E. lathyris can be cracked to useful products, making it a very valuable petrochemical feedstock from which gasoline itself can be made.

In Puerto Rico, where rum (fermented sugar cane, in other words) is one of the most important commercial products, it turns out that the Puerto Rican sugar crop is so poor these days that it is necessary to import molasses to make Puerto Rican rum; now made from Barbados molasses. The Puerto Ricans also have an energy problem, and they are developing a means of growing sugar cane for more than just rum production and have developed what they call an "energy" cane (Fig. 7), a cane which produces two or three time more dry matter per acre than ordinary sugar cane and the same amount of sugar per acre.[9] The new "energy" cane has a huge mass of fiber which can be used to fuel power plants as a source of electricity. The energy cane, which is about three times as big as normal sugar cane, has one-third the amount of sugar but three times as much biomass. Therefore, there is just as much sugar produced per acre as with ordinary sugar cane, but three times as much fuel (bagasse) is produced for power production. This has been one solution achieved in biomass by Puerto Rico.

Different kinds of plants, of course, produce differing amounts of biomass (Fig. 8), four different kinds of plants as energy sources in different parts of the world. The energy cane, Puerto Rico, is now about 100 dry tons/acre with a relatively high water requirement, with a larger production of cellulosic material. Corn which is one of the candidates in the United States for biomass is actually a pretty poor candidate, and, in addition, it is a food crop. The corn, which has starch and protein,

is used as food for animals which in turn feed people, which is a very inefficient way to feed people. Note that in the case of Euphorbia lathyris, it produces both hydrocarbon and ethanol, and I have calculated the liquid fuel yield in terms of tonnage, but the water requirement for its growth is much less than either kind of cane and is about the same as for corn, but the productivity is much higher. In terms of energy in liquid fuel in Btu/acre/year/inch of water the Euphorbia lathyris is really one of the best plants we have found, that is, 0.8 MBtu of oil and 0.8 MBtu of alcohol, making a total of 1.6 MBtu. When both the oil and alcohol are put together, there is no question that E. lathyris is twice as good as the other three crops with which is is compared.[10] The information in the above figure is based on water requirement, and you can see that the overall water requirement for E. lathyris quite low, which means it can be grown in regions of our country that are not useful for other purposes.[11] E. lathyris can grow on poor soil, and minimum water requirement. In actuality, E. lathyris can be grown with as little as 12 inches of water per year, with a slight reduction in productivity, but the oil and sugar content will be about the same. We have selected the E. lathyris primarily because it is capable of growing on land that cannot be used in the customary way for food crops.

What other kinds of plant resources can we find? The E. lathyris is only one species of a genus which has at least 2000 species which will grow in a variety of climates, and it remains for each country and each area to select that particular species best suited for that country.

There is one hitch to such a plant as E. lathyris. It must be planted each year and cut, and most of the material that is in that plant (minerals) are removed from the soil and must be replaced. When you disturb the soil there is a certain amount of loss in terms of washing away, and there will

be further depletion, even in marginal areas, if no organic matter is returned to the soil on a regular basis. Therefore, I hesitate to recommend this type of crop indefinitely, even for the next hundred years.

OTHER HYDROCARBON-PRODUCING PLANTS

What I would like to find is a tree, like the rubber tree or maple tree, which can be tapped for the removal of only the desired product; that sounds like a wild dream, except there is such a tree in Brazil. The oil from such a tree was initially shown to us in Fortaleza, in northeast Brazil where someone showed us a small bottle of oil and told us that it came from a tree, and explained how the oil was obtained. The oil was analyzed (it had been previously analyzed by others)[12] by our laboratory in Berkeley[6] and a couple of years later we went to the Ducke Forest in Manaus and saw these diesel-oil producing trees (Fig. 9). A 2-4 cm hole is drilled into the trunk of the tree and a tube inserted. A bucket is placed under the tube to catch the oil as it drips down. This is done twice each year, and the material can be used directly, either as a component in pharmaceuticals, or other uses by the natives in Brazil, or put directly into a car, without any modification whatsoever. The components of that oil are shown in Fig. 10 which is a gas chromatogram of the oil,[12] and there are 24 easily recognized components and they all have the same number of carbon atoms, 15 carbon atoms/molecule, all made from the same starting material, farnesyl pyrophosphate, which is, in turn, made from isoprene, a five-carbon unit. The question is whether it would be possible to grow a tree which would produce this type of material here in the United States. This tree, the Copaifera multijuga, is a tropical tree, and we have seen species of this genus as far north as Puerto Rico. Perhaps it could be

grown in southern Florida, but I am unaware if any are growing on the continental United States.

There are several other oils which can be harvested from trees, but the oil from the Copaiba has the best characteristics as a fuel and raw material. Other oils are shown in Fig. 11, the black oil being from Euphorbia lathyris; it is black and sticky in a way similar to crude oil. The yellow oil is from C. langsdorfii, and the one common in the Amazon is C. multijuga. The next is another oil, marmeleiro, again from Brazil, obtained by steam distilling the dry plant (bush or small tree), a Croton (another Euphorbia), and the oil is mostly composed of $C_{10}$ rather than $C_{15}$ as in the Copaiba oil. The next one is from jojoba, a different family, which is a seed oil, an ester, not a hydrocarbon. Another Brazilian seed oil is also show, Andiroba oil, which is a lipid, and the one on the far right is from a seedpod, Pittosporum undulatum, which grows very widely in California. The seed is in a fruit about the size of a kumquat, with small seeds inside. The oil from the Pittosporum is in the seedpod itself, i.e., from the fruit, and that is almost entirely terpenoid in character. The oil from the C. multijuga is so clean when it comes out of the tree and is all $C_{15}$ in composition and it is the right volatility for a diesel engine. It may go directly into an automobile engine. There are several species of the Copaifera and they all produce a similar material. The closest thing to the Copaiba oil is the oil from the P. undulatum here in the United States, but it would not be an edible oil, it is a hydrocarbon, more like turpentine than like the soybean oil.

We learned about Pittosporum as a possible plant candidate because someone in the Philippines sent us some Pittosporum resiniferum seeds (petroleum nuts), which has fairly large seeds, which are sometimes tied

to the end of a stick and lit, and used for a torch (Fig. 12); the seeds of the P. resiniferum have quite a bit of oil in them and can be used for illumination.[13] The chemistry of the P. resiniferum is shown in Fig. 13, mostly myrcene and pinene, with a little nonane and heptane.[14]

GENETIC ENGINEERING FOR HYDROCARBONS

I would like to discuss the biosynthetic route to terpenes (Fig. 14 a & b), with IPP (isopentenyl pyrophosphate), and dimethylallylprophophate (DMAPP) which come together to make a $C_{10}$ compound, which has the same allylic structural component as the DMAPP, and if you add another molecule of IPP you get a $C_{15}$ compound, etc. The black oil from E. lathyris goes as far as farnesyl pyrophosphate and then doubles up to squalene, losing both pyrophosphate groups, so the chain stops growing, cyclizes, and stops at the $C_{30}$, and is the source of triterpenes. The oil in the Copaifera multijuga is made by cyclizing the $C_{15}$ farnesyl pyrophosphate to form all the sesquiterpenes. In the Pittosporum, the reaction stops at $C_{10}$, monoterpenes. There are small amounts of $C_{20}$ and $C_{40}$ in all the oils.

We would like to be able to stop the reaction in the plant at this point, i.e., find a species of plant(s) that would make terpenoid compounds only, particularly sesquiterpenes, which are the most valuable compounds from the point of view of end products.[6, 7] This seems to require a single gene transfer. If it were possible to remove the gene from the Copiafera tree which provides the cyclic $C_{15}$ component, and shut it off this way, perhaps we could have the E. lathyris producing the diesel-oil like material similar to that obtained from the C. multijuga, for example. This could be done by genetic engineering (Fig. 15). The enzyme could be removed from the Copaifera and partially sequenced from this polynucleotide probe would be built to extract the gene DNA for the enzyme. The DNA for that enzyme

would go into a suitable plasmid vector. The plasmid could be inserted into a selected plant cell, such as one from E. lathyris, and the cell, in turn, could be used as the basis for the whole plant. The seedlings of the Copaifera species (Fig. 16) grown in the laboratory could be used as a source of the enzyme to be inserted into the E. lathyris. We are now learning to grow E. lathyris as single cells in tissue culture (Fig. 17), and the leaf shoots generated from the callus are shown in Fig. 18. The callus is a mass of undifferentiated cells made from single protoplasts We are now on our way back from a single cell of the E. lathyris toward plant regeneration. The leaflets from the callus show that we are now on the way to regrowing the E. lathyris plant from single cells.

ARTIFICAL PHOTOSYNTHESIS

We will now take a few minutes to discuss the other route to alternative energy sources, that is, to use the knowledge of the green plant quantum conversion apparatus to try and build a totally synthetic device for solar energy conversion.[15] The green plant uses the chloroplast (Fig. 19) to convert the quanta into chemical energy, depending on the laminar structure of the membrane. The two sides of the membrance in the chloroplast seem to perform two quantum acts (Fig. 20), one quantum is absorbed on one side, taking an electron away from water to make oxygen and that electron is raised to some mediate level from which it falls, making ATP on the way. The electron then is raised by a second quantum to a still higher level so that it can produce molecular hydrogen under proper circumstances. The electron can now be used to reduce the carbon dioxide and then go on to sugar, hydrocarbons, proteins, etc. If some plants do not receive $CO_2$ the electron at this point will come off as molecular hydrogen. We propose to construct a membrane synthetically. The electron

would pass from water on the inside of the membrane out to the other side, with proper sensitizers and catalysts on both sides. We need two sides, and the membrane is used to separate the oxidation and reduction products. Our first effort is to demonstrate that we can photochemically transfer an electron across a membrane which separates the oxidation product from the reduction product. The manganese on one side of the membrane helps to generate the oxygen, through the first quantum act, it then falls back down and there is the second quantum act, with the acceptor on the other side, an iron-sulfur compound, where finally it is possible to generate hydrogen. We have to transfer the electron right through the membrane. The scheme for photosensitized electron transfer across a lipid vesicle wall has been worked out (Fig. 21). The two curved lines represent the two membrane surfaces, made of phospholipid; and we put onto that membrane a sensitizer on both sides, and when we shine light on the sensitizer, it becomes an excited state which can hand an electron to the water soluble acceptor ($HV^{+2}$), which becomes reduced, and the sensitizer on the outside the vesicle membrane is oxidized. We then have the sensitizer on the outside in a different valence state than the sensitizer on the inside of the vesicle. This is followed by an isoelectronic exchange reaction, producing ruthenium$^{+3}$ on the inside and ruthenium$^{+2}$ on the outside. The ruthenium$^{+3}$ is a very interesting oxidizing agent, which with a catalyst, can oxidize water, to generate oxygen. Our first experiments were done with an irreversible donor (EDTA) which regenerates the ruthenium$^{+2}$ on the inside of the membrane.

If we can show that shining light on this system, with EDTA on the inside of the membrane and the other material (viologen) on the outside without platinum present, the color change of the viologen will indicate

that we have transferred an electron across the membrane. The cofactors in the photoelectron transfer reactions across the membrane are indicated in Fig. 22. Here light is shone on the system, and blue viologen is formed on the outside; and since the EDTA cannot reach it, we know that the electron has crossed the membrane. The purpose of this experiment was not to generate oxygen, but to show that we have transferred an electron photochemically across a membrane.

If platinum is placed on the outside with the viologen, you get hydrogen, and if you replace the EDTA with ruthenium oxide catalyst, you can get oxygen on one side and hydrogen on the other. In Fig. 23 is the big thick membrane, the hollow fiber treated membrane. A prototype for laboratory device, is shown with the treated fibers in Fig. 24 which is a laboratory apparatus, containing the treated fibers, and we can begin to try and make this work. When the dyestuff is buried in the membrane the electron donors and acceptors cannot easily get at it. We are also having some difficulty in pushing water through the tube of the hollow fibre because of some mechanical collapse during the dying process. But these problems should be overcome shortly.

## CONCLUSION

Thus it appears that certain green plants could be developed immediately for the production of liquid fuels and materials, particularly hydrocarbons and fermentable carbohydrates. In the more distant future--a decade or so--we can look forward to the construction of totally synthetic devices for the capture and conversion of quanta from the sun into stable chemical forms of interest both as fuels and raw materials.

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## FIGURE CAPTIONS

Figure 1 US energy sources and uses, 1980

Figure 2 Energy gains and costs for high and low drilling intensity

Figure 3 $CO_2$ concentration at Muano Loa (thru 1980)

Figure 4 E. lathyris, Davis, showing irrigation effect on plant size

Figure 5 Conceptual processing sequence to recover terpenoids and sugars from E. lathyris

Figure 6 Catalytic cracking pattern of oil from E. lathyris

Figure 7 Energy cane, Puerto Rico

Figure 8 Comparison of energy yields for different crops

Figure 9 Copaifera multijuga, Manaus, showing diesel oil from bung

Figure 10 Chromatogram of Copaiba oil

Figure 11 Various plant/tree oils

Figure 12 Pittosporum resiniferum nut burning

Figure 13 GLC of extract from Pittosporum resiniferum

Figure 14 Terpenoid biosynthesis

Figure 15 Manmade evolution (genetic engineering)

Figure 16 C. langsdorfii, C. officinals, Melvin Calvin Laboratory

Figure 17 E. lathyris callus, Melvin Calvin Laboratory

Figure 18 E. lathyris shoots from leaf protoplast, Redenbaugh & Kawaguchi, Plant Genetics, Inc.

Figure 19 Electron micrograph of chloroplast lamallae

Figure 20 Photosynthetic electron transfer scheme (Z-scheme)

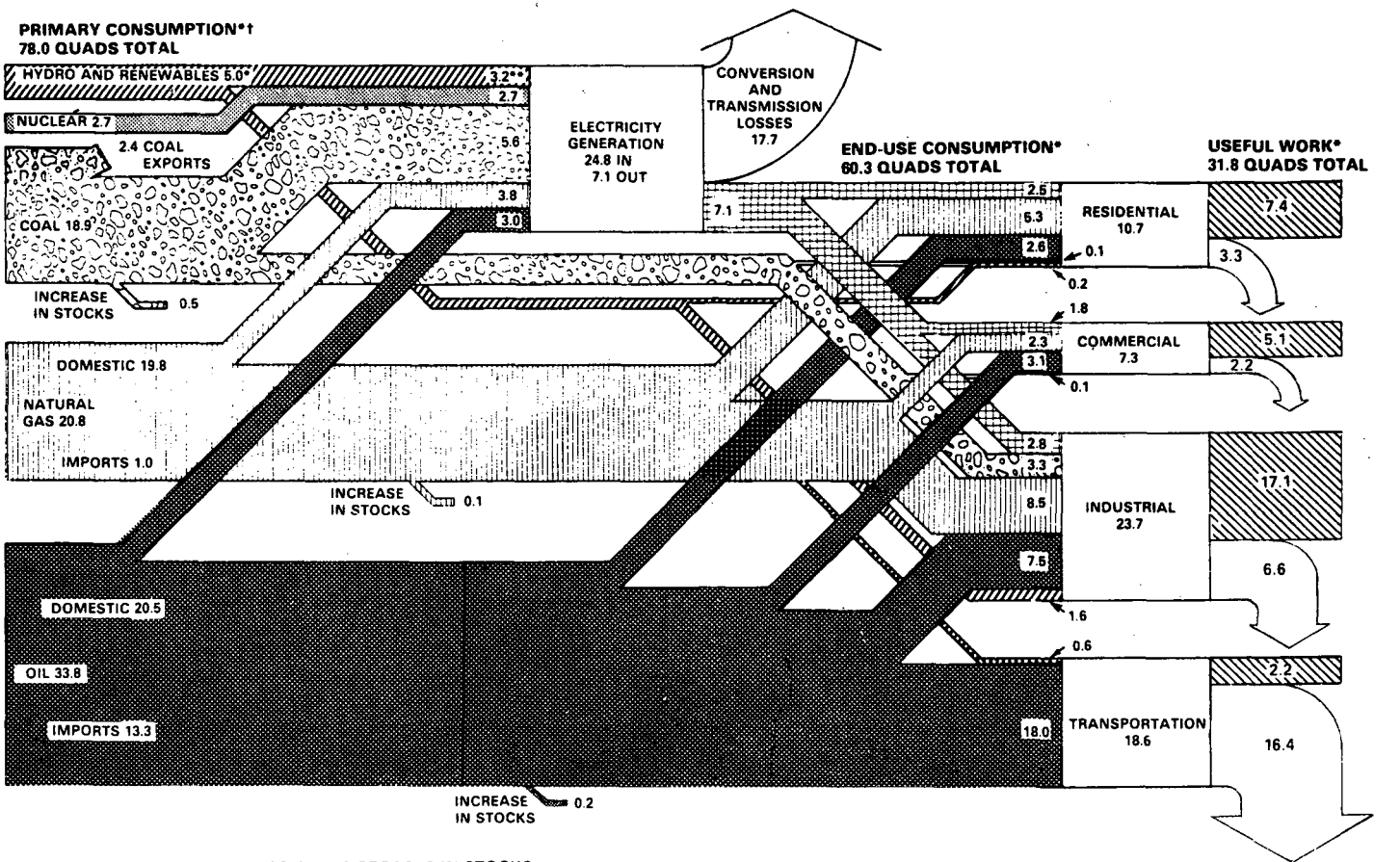
Figure 21 Scheme for photosensitized electron transfer across a lipid vesicle wall

Figure 22 Cofactors in photoelectron transfer reactions across a membrane

Figure 23 Treated hollow fiber, ZnTPP-acetone, 5X

Figure 24 Hollow fiber apparatus

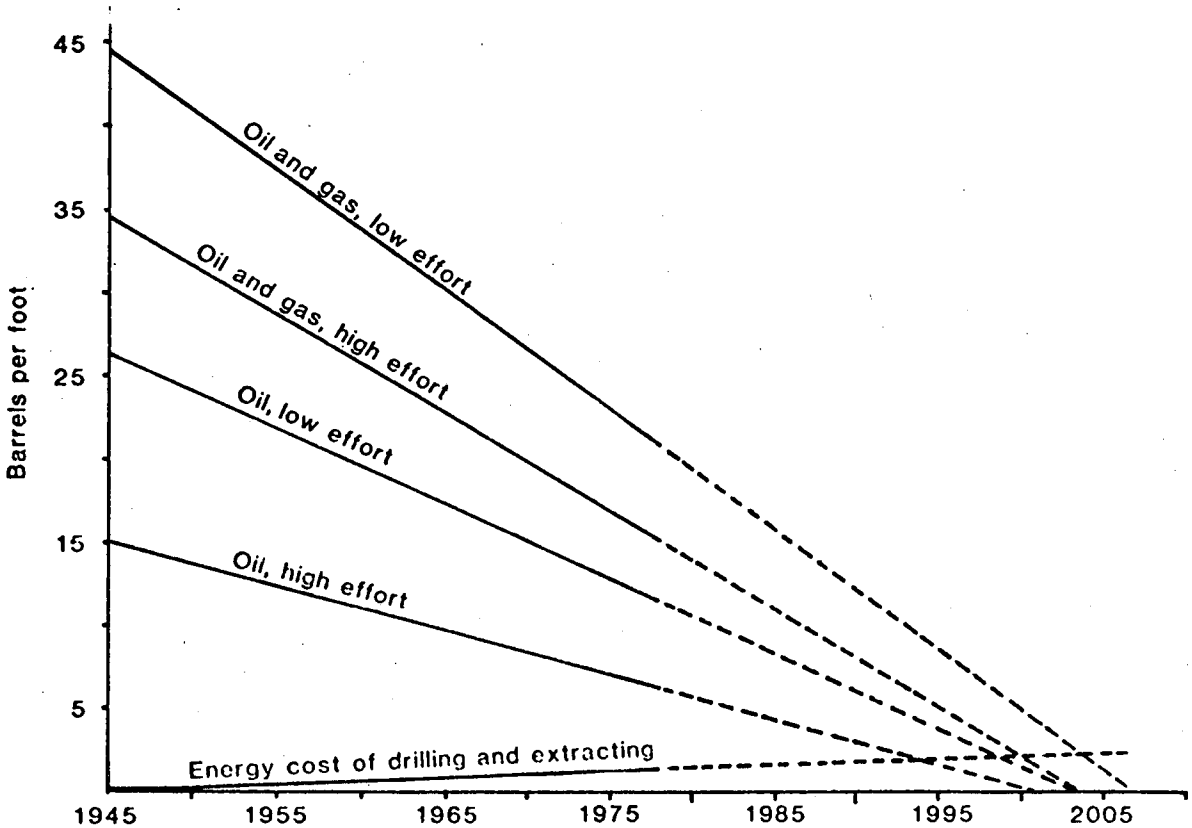
## U.S. ENERGY SOURCES AND USES IN 1980
(IN QUADRILLIONS OF BTUs)




† EXCLUDING COAL EXPORTS AND INCREASES IN STOCKS
* INCLUDES 1.8 QUADS OF BIOMASS USE NOT CURRENTLY ACCOUNTED FOR IN DOE STATISTICS
** INCLUDES 0.2 QUADS OF IMPORTED HYDROELECTRIC POWER
*** BASED ON END-USE EFFICIENCIES FROM 1979 BROOKHAVEN DATA

Fig. 1

XBL 818-11422




Linear extrapolations (dashed lines) of energy gains and energy costs for high and low drilling intensity. (Hall, 1981)

XBL 813-8448

Fig. 2

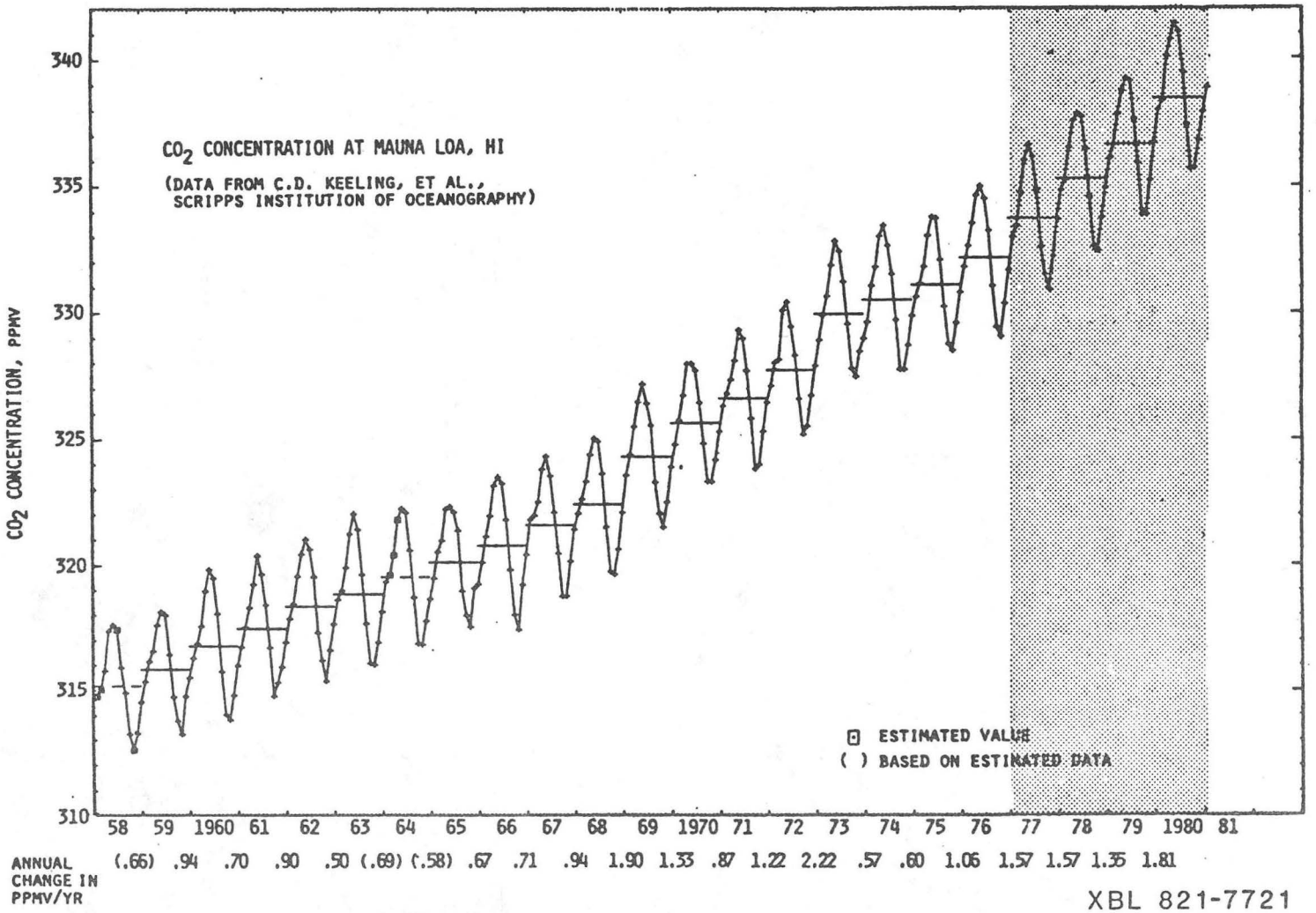



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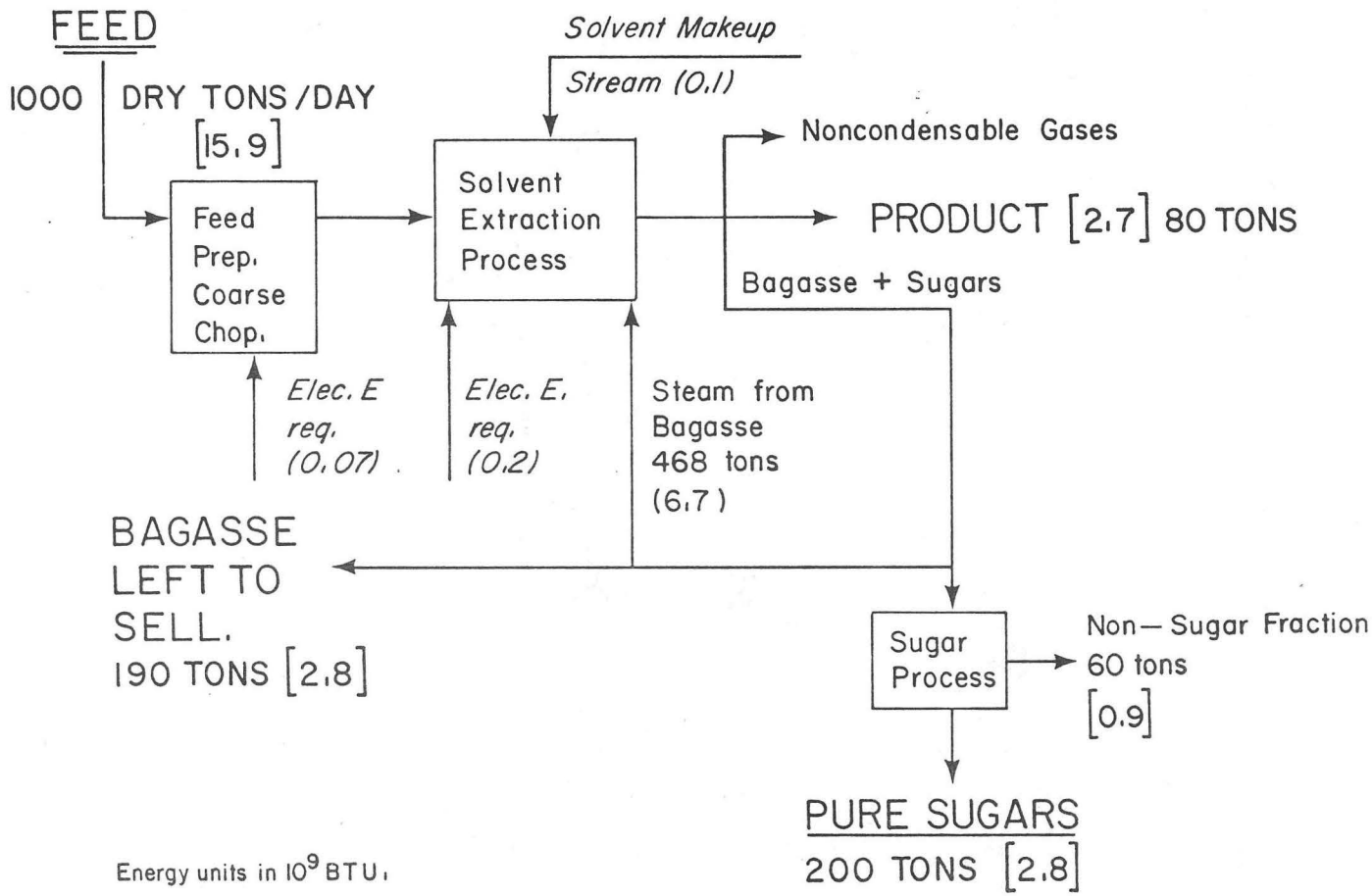
Fig. 3

CBB 800-13496

Fig. 4

Fig. 5

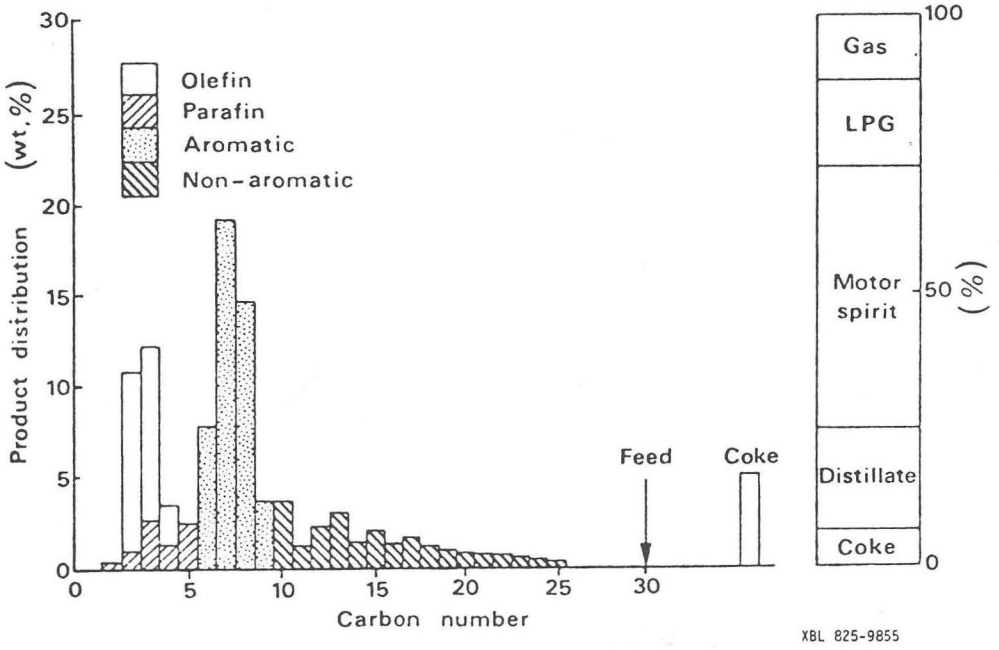
Conceptual Processing Sequence to Recover Terpenoids and Sugars from Euphorbia lathyris




XBL 807-4263A

Fig. 6

Products of conversion over Mobil zeolite catalyst of Euphorbia lathyris terpenoids (heptane soluble) (adapted from Nemethy et al 1980).



CBB 822-1649

Fig. 7

Fig. 8

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 | $16 \times 10^6$ BTU (0.64 tons) | 25 | 0.65 | $44.2 \times 10^6$ BTU (3.4 tons) | 1.77 |
| SUGAR CANE TO ETHANOL | 30 | $60 \times 10^6$ BTU (2.4 tons) | 78 | 0.78 | $312 \times 10^6$ BTU (24 tons) | 4 |
| ENERGY CANE TO ETHANOL | 35 – 50 | $65 \times 10^6$ BTU (2.56 tons) | 48 | 0.35 | $400 \times 10^6$ BTU (31 tons) | 8.2 |
| EUPHORBIA LATHYRIS TO HYDROCARBON AND ETHANOL | 8.5 | $20 \times 10^6$ BTU (0.58 tons)<br>$17.3 \times 10^6$ BTU (0.68 tons) | 25 | 0.82<br>0.78 | $79.6 \times 10^6$ BTU (6.12 tons) | 3.2 |

XBL 813-4492

Fig. 9 CBB 821-230

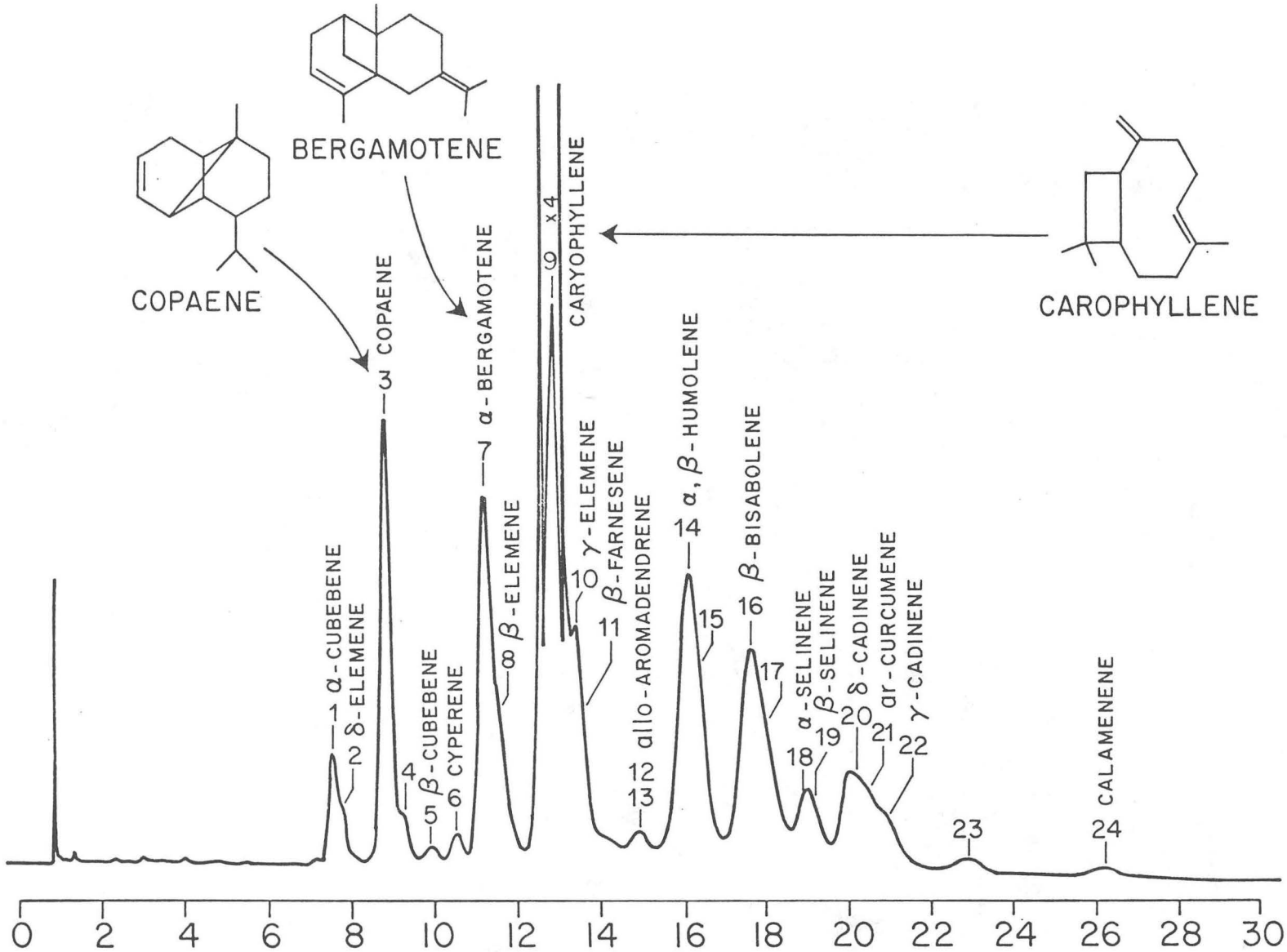



Fig. 10

Wenninger, Yates & Dolinsky,
J. Amer. Oil Chem. Soc. 50,
1304 (1967)

XBL798-4998

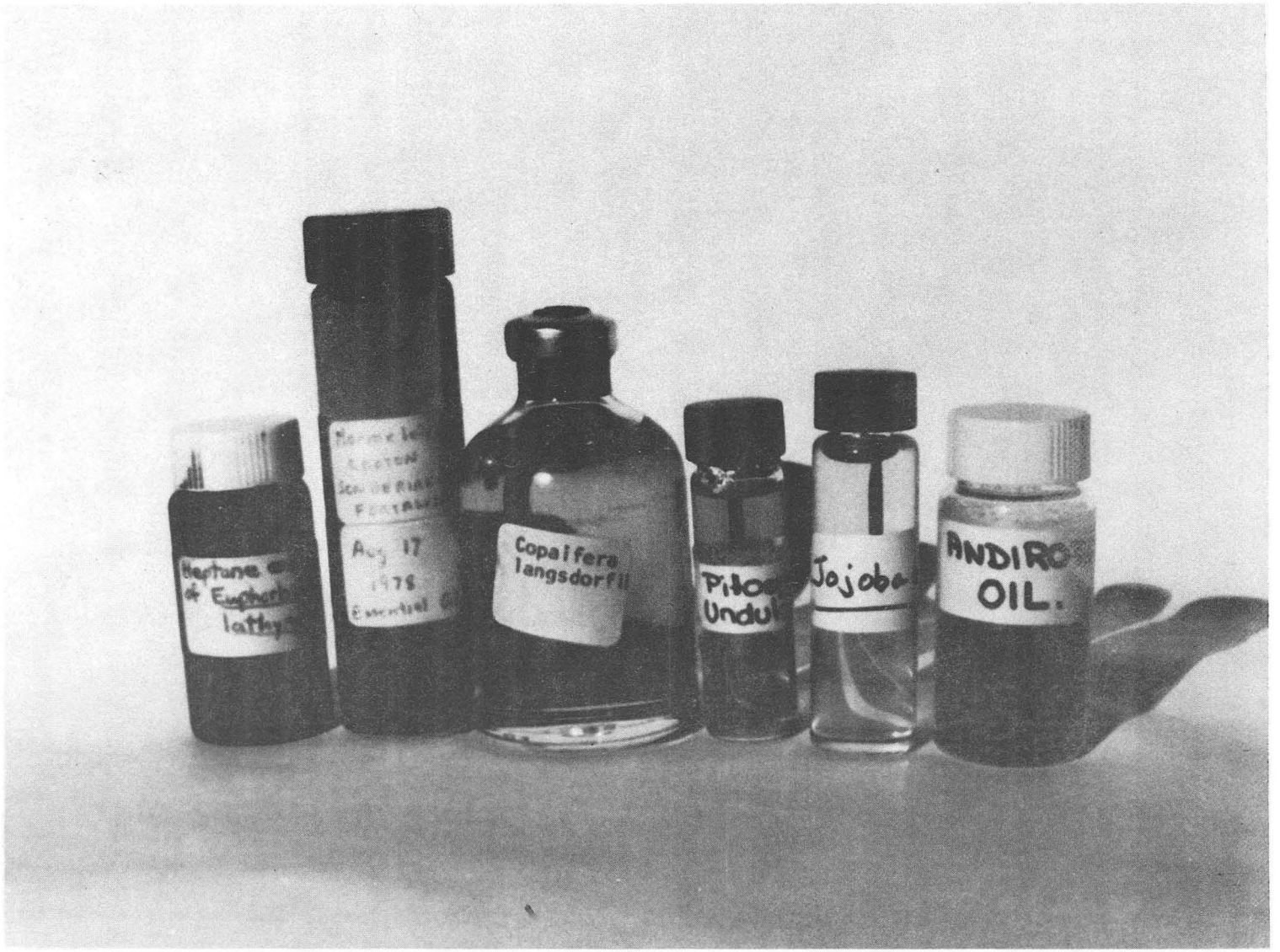



Fig. 11

CBB 822-1208

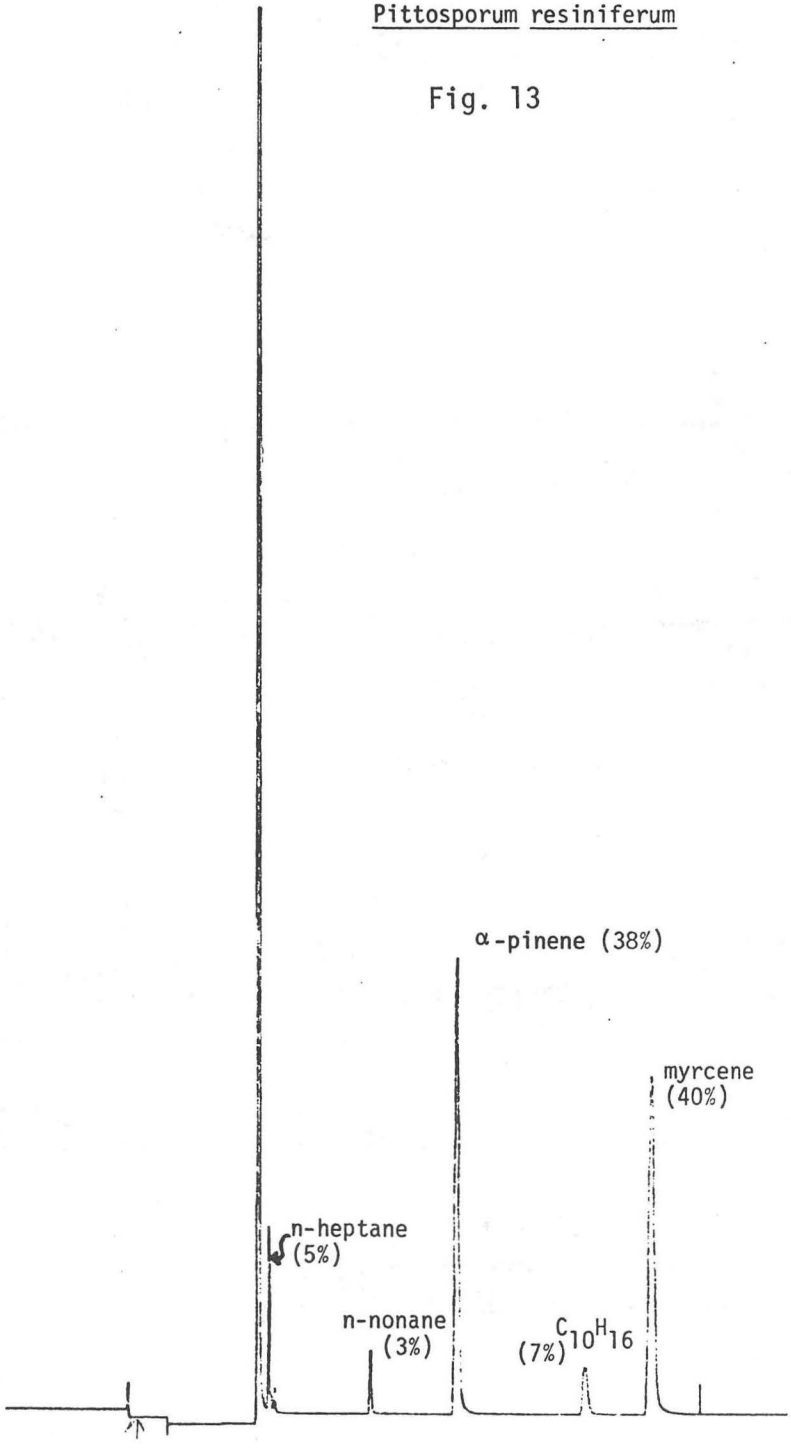
Fig. 12

CBB 819-8416

GLC OF EXTRACT FROM

Pittosporum resiniferum

Fig. 13

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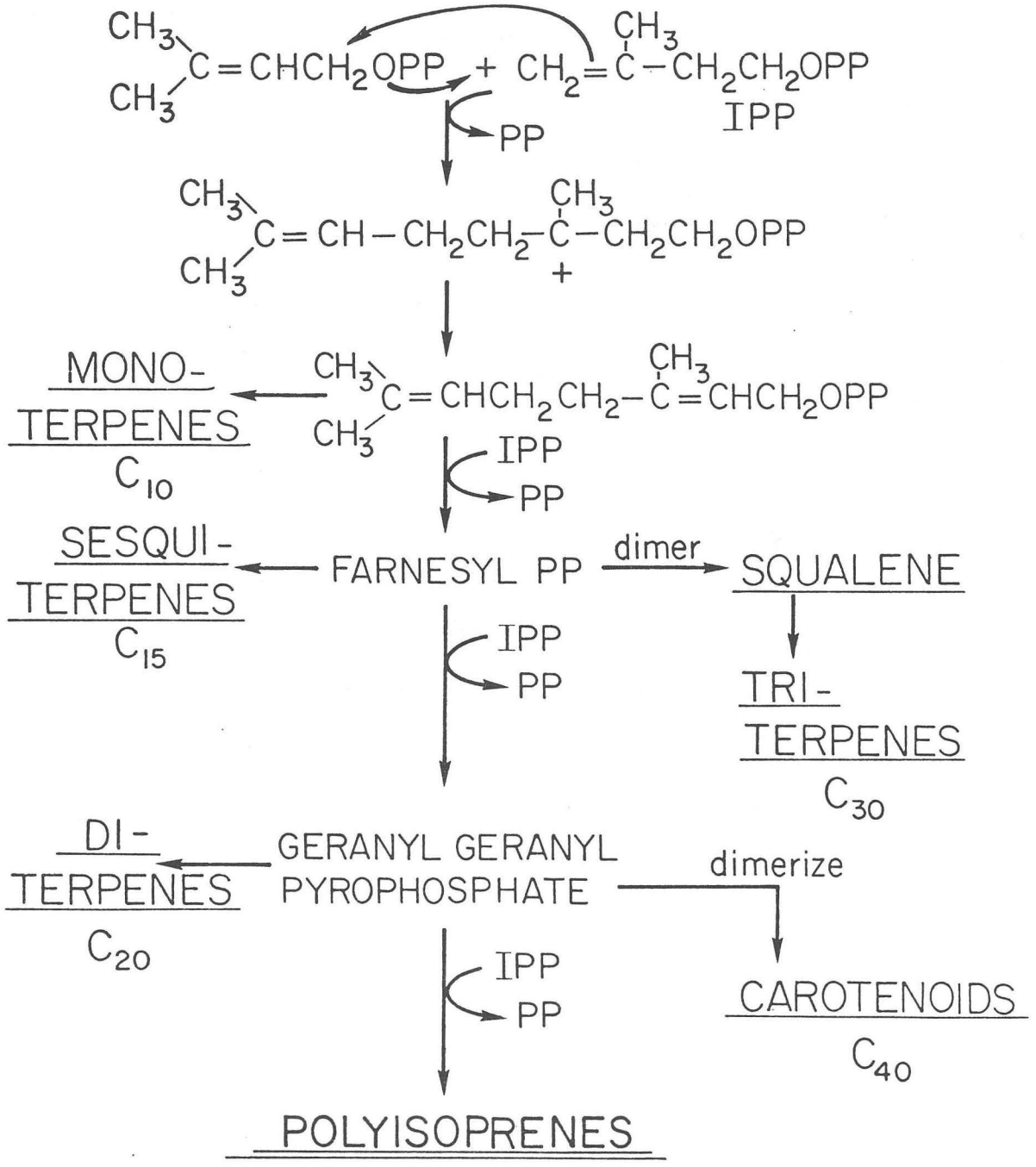


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Fig. 14

# Man Made Evolution

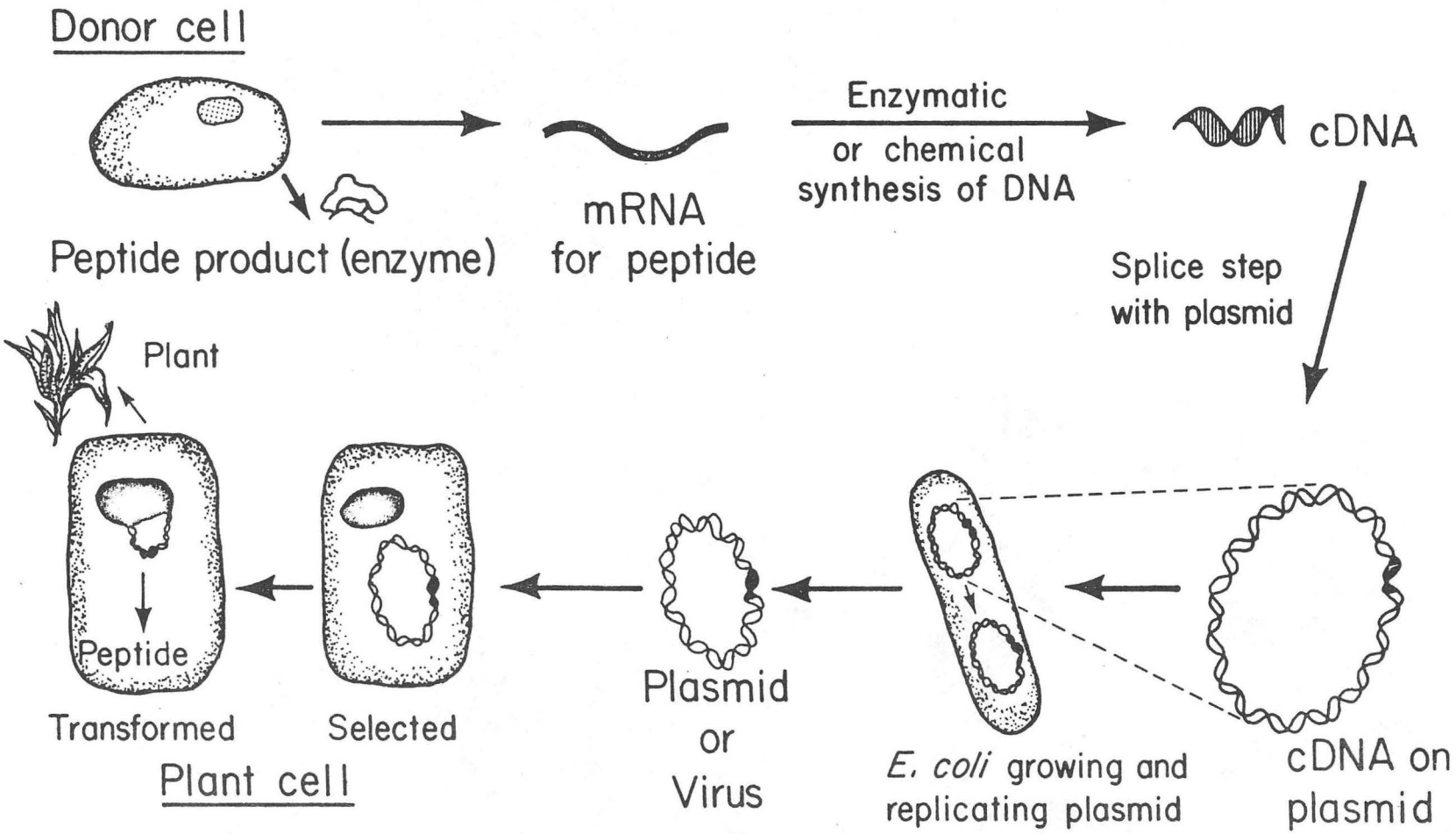



Fig. 15

XBL 804-4127

C. langsdorfii
Planted 12/8/80
Picture taken 8/5/81

C. officinalis
Planted 4/13/81
Picture taken 8/5/81

Baysdorfer

Fig. 16

CBB 818-7824

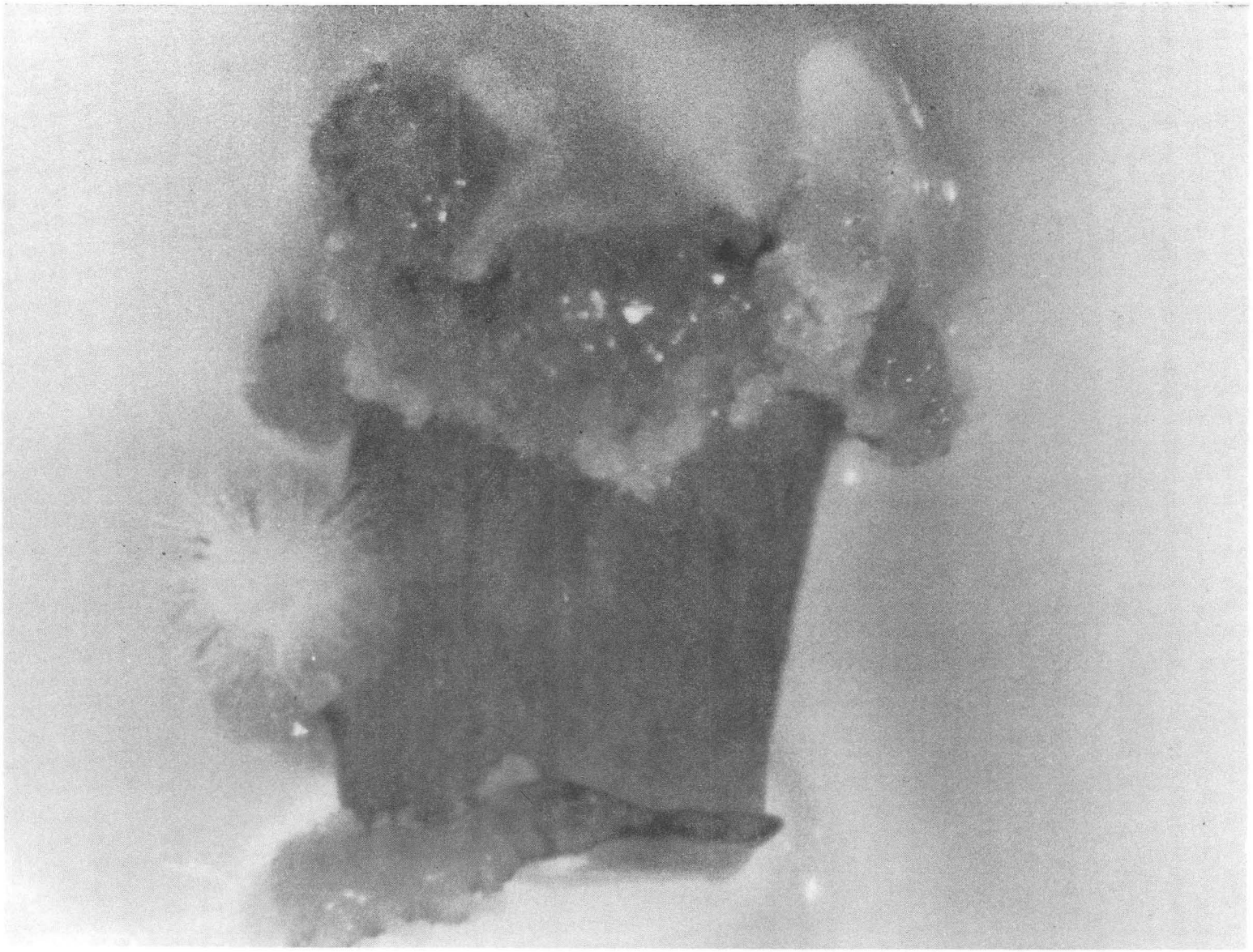


Fig. 17

CBB 814-3452

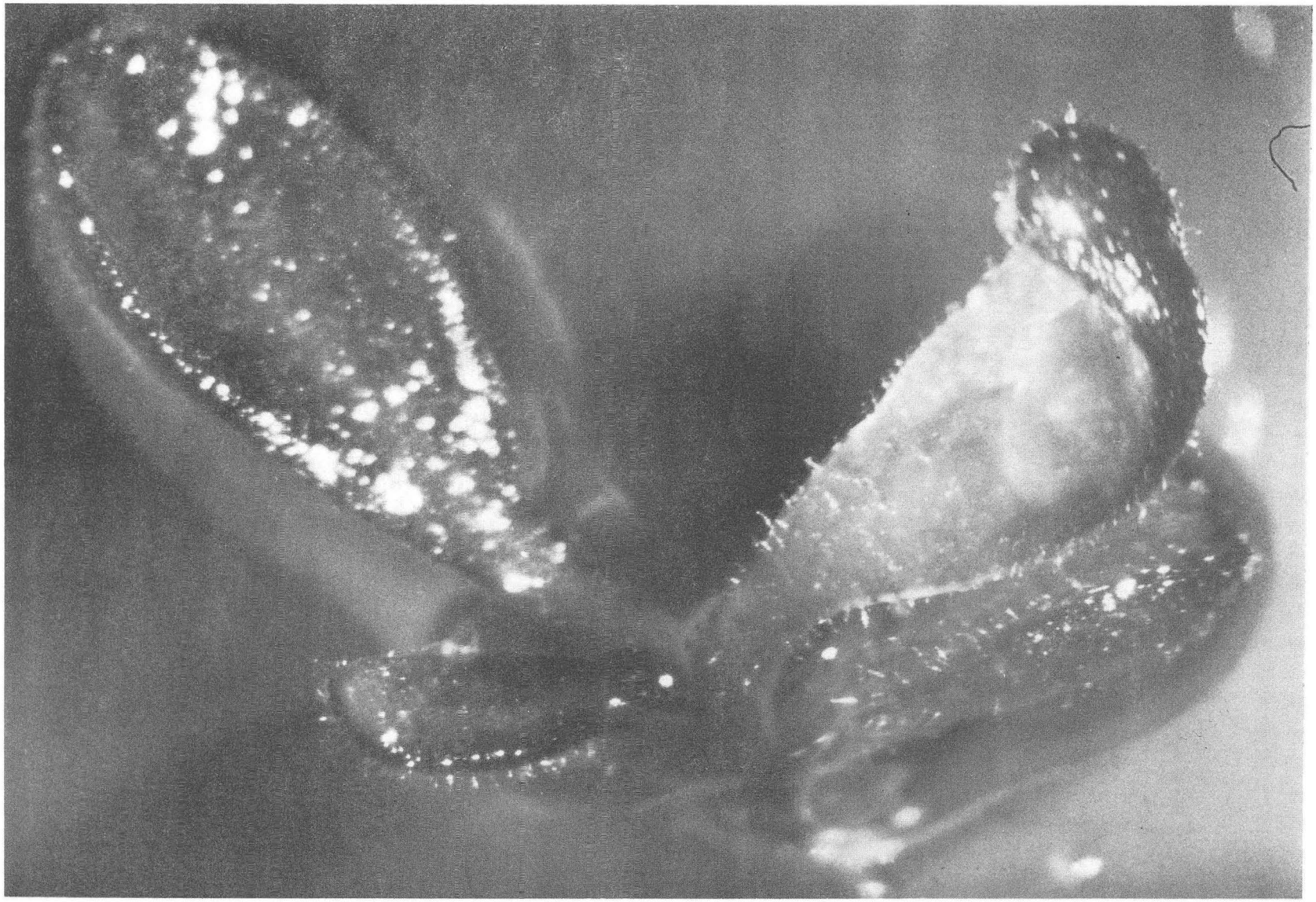
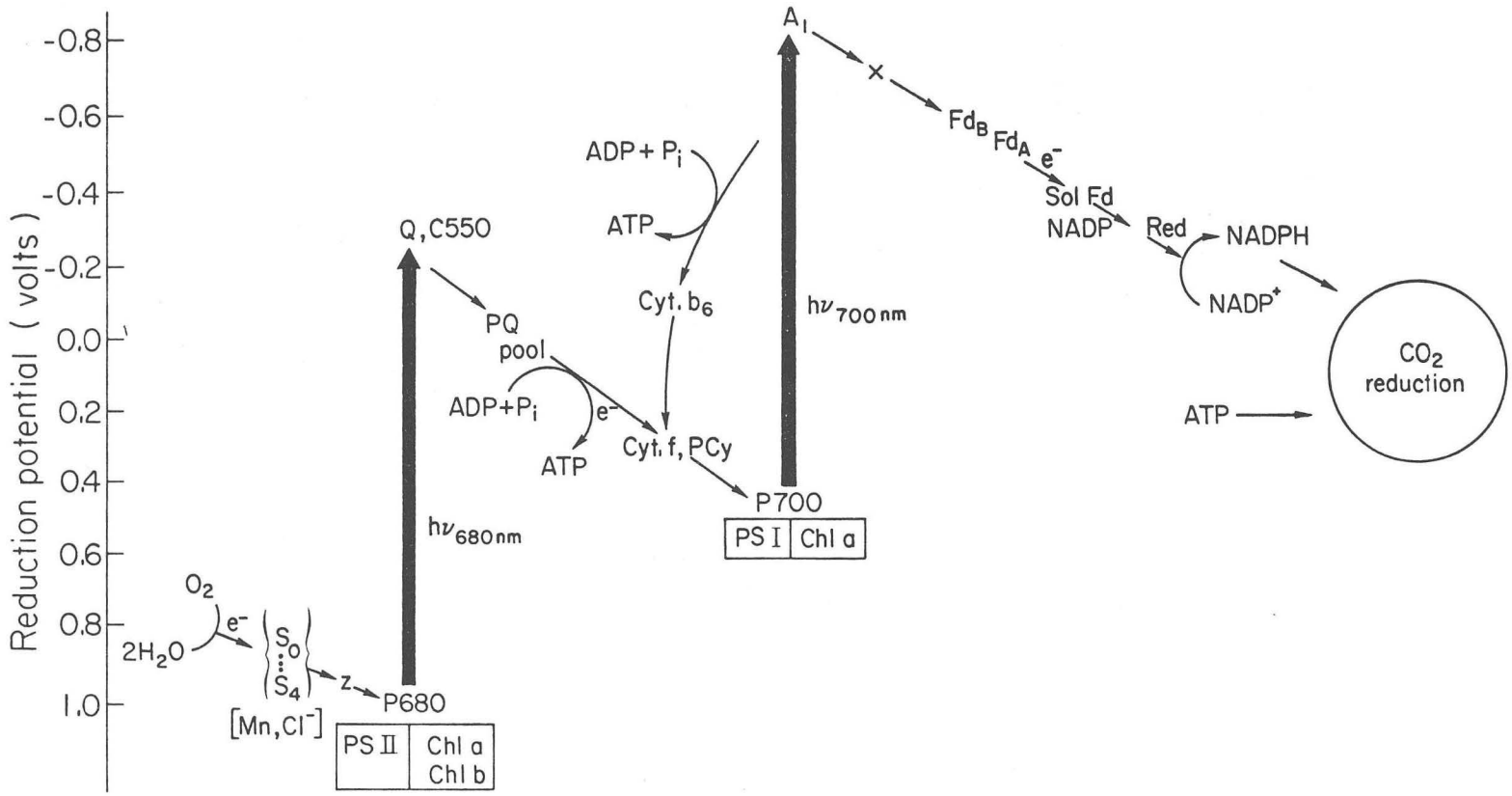


Fig. 18

CBB 829-8432

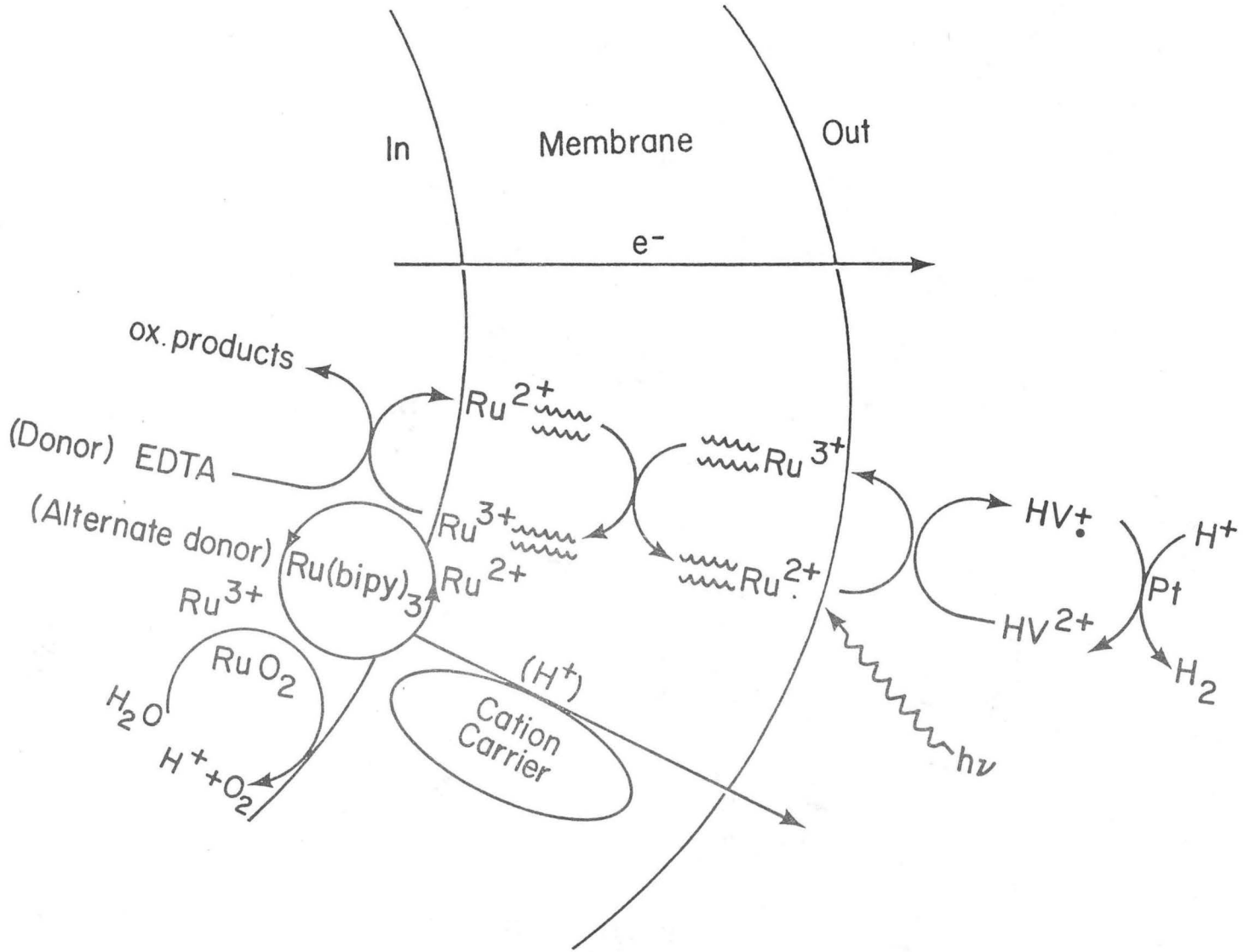
XBB 741-7523

Fig. 19




XBL797-4937

Fig. 20



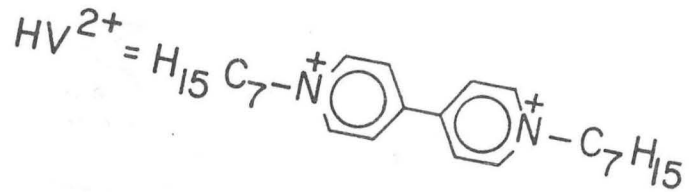
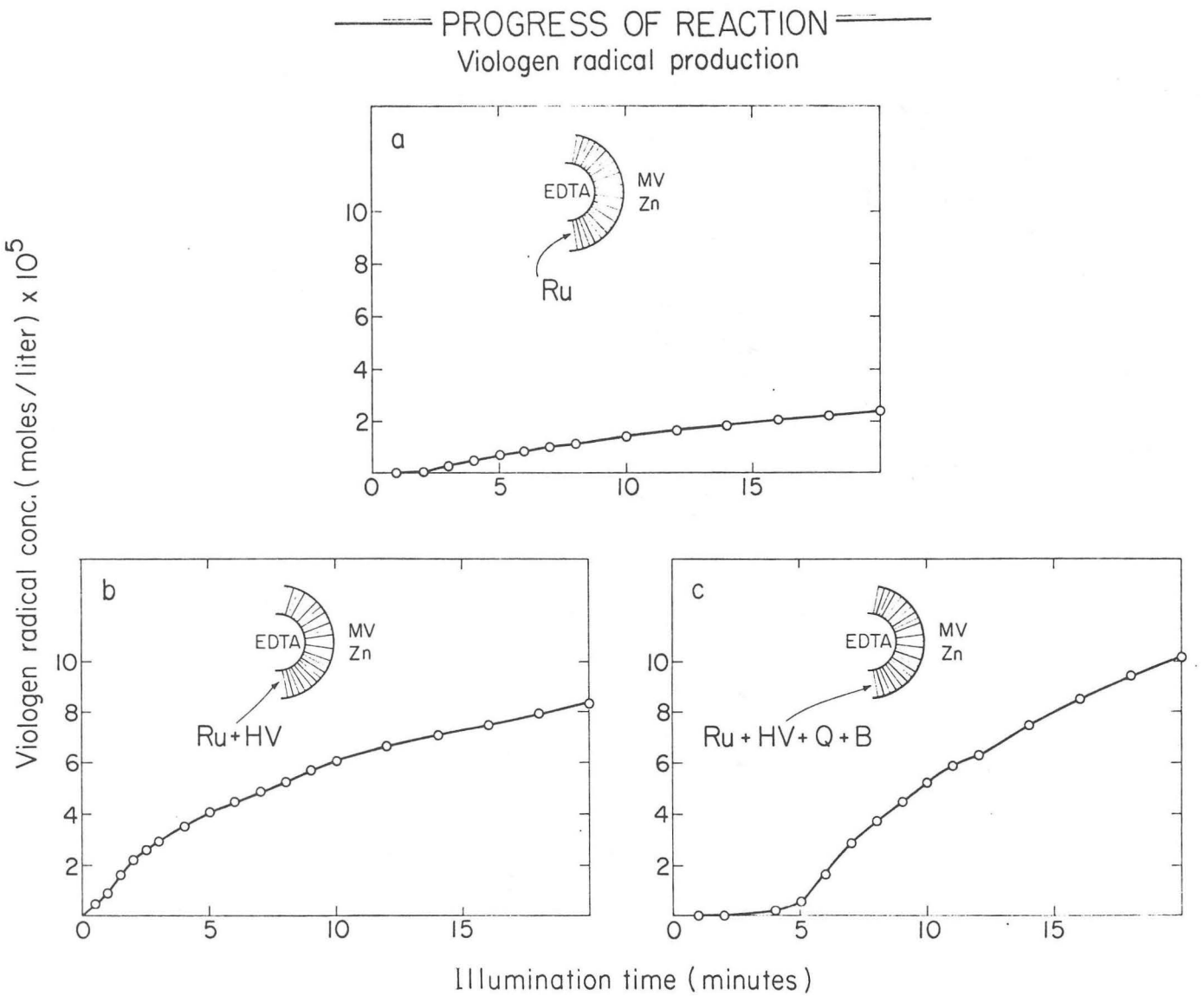



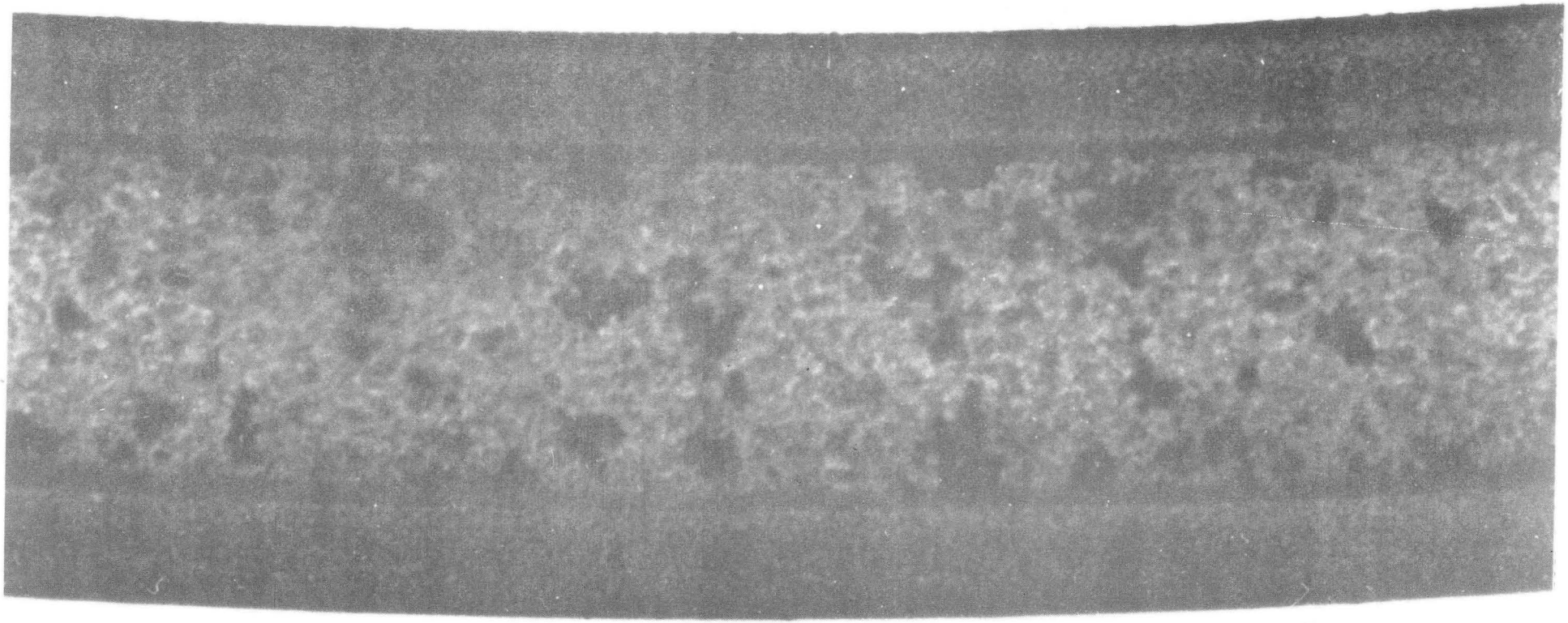

Fig. 21

XBL 821-61



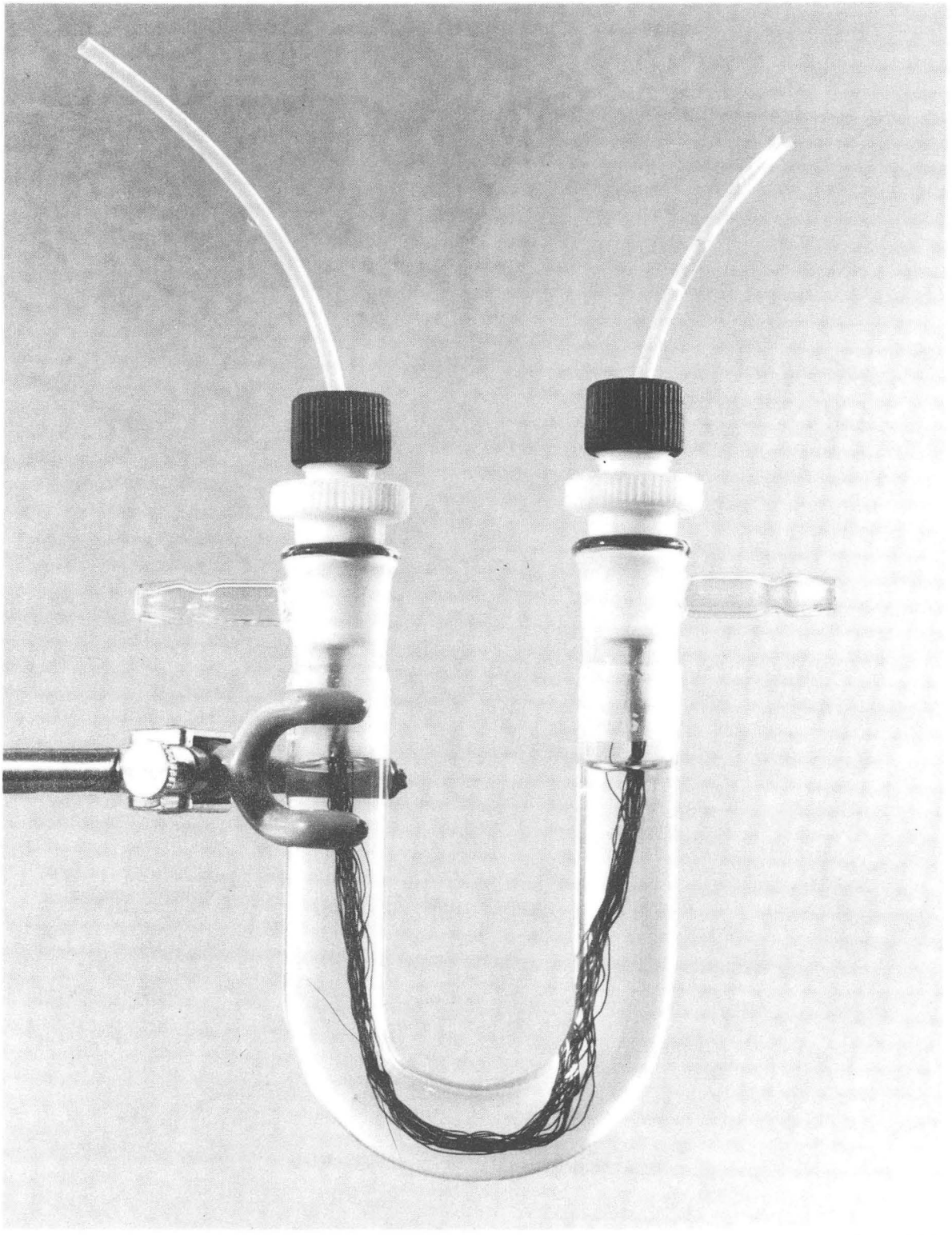

XBL 791-4643

Fig. 22



BBC 813-2202

Fig. 23



CBB 814-3554

Fig. 24

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