# BIO-RENEWABLE SOURCES OF CHEMICALS AND FUEL IN THE CHIHUAHUAN DESERT

# ROBERT P. ADAMS

Science Research Center-Utah, Hardin-Simmons University, 8555 S. Escalante Drive, Sandy, Utah 84092 USA

### ABSTRACT

The Chihuahuan Desert could be the source of several important chemicals including natural rubber, hard waxes, liquid waxes, water soluble gums, diterpene acids, soaps, antioxidants, tannins and biologically active compounds. The evolution of secondary compounds is discussed in context with the Chihuahuan Desert environment. Fuels from desert plants do not appear promising at this time. However, several species that produce chemicals for direct utilization or for use as feedstocks do have considerable merit. These crops are examined for their products, markets, production and problems in domestication. The renewable sources of chemicals discussed are: guayule (Parthenium argentatum) (natural rubber); candelilla (Euphorbia antisyphilitica) (hard waxes); jojoba (Simmondsia chinensis) (liquid waxes); Acacia spp. and Astragalus spp. (Fabaceae) (water soluble gums); Grindelia spp. and Chrysothamnus spp. (Asteraceae) (diterpene acids); Yucca spp. (Agavaceae) (soaps); Larrea spp. (Zygophyllaceae) (antioxidants); Acacia spp. (tannins) and various other species for biologically active compounds.

## RESUMEN

El Desierto de Chihuahua podría ser fuente de varios productos químicos importantes, incluyendo goma natural, ceras sólidas, ceras líquidas, gomas hidrosolubles, ácidos diterpénicos, jabones, antioxidantes, tanino, y compuestos biológicamente activos. Se discute la evolución de compuestos secundarios en contexto con el ambiente del Desierto de Chihuahua. Los combustibles provenientes de plantas del desierto no ofrecen ahora promesa económica. Sin embargo, hay varias especies de mucho mérito que producen compuestos químicos para su utilización directa, o para uso de forrajes. Se examinan estas plantas por sus productos, sus usos comerciales, producción y problemas en la domesticación. Las fuentes renovables que se discuten son: guayule (Parthenium argentatum) (goma natural); candelilla (Euphorbia antisyphilitica) (ceras sólidas); jojoba (Simmondsia chinensis) (ceras líquidas); especies de Acacia y Astragalus (Fabaceae) (gomas hidrosolubles); especies de Grindelia y Chrysothamnus (Asteraceae) (ácidos diterpénicos); Yucca (Agavaceae) (jabones); Larrea (Zygophyllaceae) (antioxidantes); Acacia (taninos) y varias otras especies para compuestos biológicamente activos.

The Chihuahuan Desert is an area noted for an abundance of space, sunshine, and xeric conditions. In this ecosystem there has been a long co-evolutionary battle for survival among plants, animals, and microorganisms. During this period plants have evolved numerous defenses against the xeric conditions that include: thick, waxy cuticles on leaves and stems to decrease transpiration (candelilla [Euphorbia antisyphilitica],

cacti [Cactaceae], yuccas [Yucca spp.]); succulent leaves and/or stems (cacti); deciduous leaves (ocotillo [Fouquieria splendens]); deep roots that reach lower water tables (mesquite [Prosopis spp.]); and spines and surface pubescence that slow surface air movements and transpiration (cacti).

Although xeric adaptations to stress have produced several important economic chemicals (wax and rubber for example), the co-evolutionary development of secondary compounds in plants has generated a whole series of compounds for possible commercial use. It is now becoming apparent that secondary natural products may be of considerable (or critical) importance for the survival of plants (Siegler 1977). Secondary compounds have been shown to repel herbivores, e.g., deer (Odocoileus), in the case of essential oils and chlorogenic acid (Radwan and Crouch 1978), deter browsing by hares (Lepus) (Bryant 1981), and act as toxic and feeding deterrents in insects (Stubblebine and Langenheim 1977). Cates and Rhoades (1977) hypothesize that herbivores can be divided into specialists and generalists. The specialist herbivores often prefer young leaves or rapidly growing tissues, whereas the generalists tend to prefer mature leaves and tissues (Cates and Rhoades 1977).

The generalist herbivores browse many different species and often over a considerable portion of the year. Plant species which grow in arid lands can be subdivided into two basic groups: annuals, which take advantage of infrequent rains and grow to maturity (seed production) very quickly; and perennials that have various adaptations to enable them to survive throughout the year. The annuals can escape herbivores by their ephemeral nature and by the evolution of specific toxins which are not energy intensive (Cates and Rhoades 1977). Perennials, on the other hand, are subject to disease and herbivores throughout the year. Furthermore animals in the Chihuahuan Desert have little or no dormant season. In the more temperate regions, little protection may be needed during the winter because many animals may be inactive. The driving force of evolution is survival from generation to generation. Long-lived perennials need not reproduce every year but they must survive drought, diseases, and animal browsing in order to eventually reproduce themselves. The evolution of environmental protection and/or more efficient metabolic methods is pitted against a more or less predictable selection force: natural variation in rainfall, wind, heat, and desiccation. In contrast, the evolution of plant chemical defenses races constantly with the predator in a co-evolutionary battle.

As soon as a plant evolves a new chemical or morphological defense, selection begins to operate on the predators that have mutations allowing them to overcome (e.g., detoxify) the new plant defense. The case of the monarch butterfly (*Danaus plexippus*) larvae is a good example (Fig. 1)

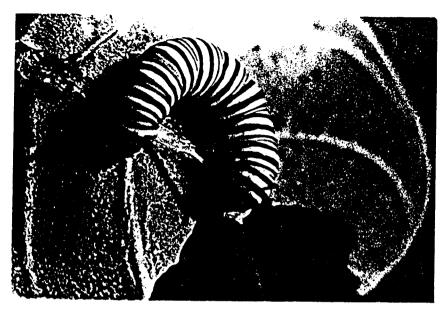


Fig. 1. Monarch butterfly (Danaus plexippus) larvae feeding on Calotropis procera (Asclepiadaceae). Cardiac glycosides are obtained from the leaves and sequestered in the larvae.

because larvae of this species sesquester the cardiac glycosides of the members of the Asclepidaceae and use these compounds as their own defense against predators (Roeske et al. 1976). Perennial Chihuahuan Desert land plants tend to have morphological defenses (e.g., spines in cactus) and/or chemical defenses (e.g., bitter tasting phenolics in creosote bush) (Rhoades 1977). In mesic regions plant species can often tolerate considerable browsing because adequate moisture is available for regrowth. This is not the case in the Chihuahuan Desert. Thus, it appears that the accumulation of considerable secondary products in many Chihuahuan Desert land plants is a necessary constraint for survival in that environment. Since plants have evolved (and co-evolved) defenses in the Chihuahuan Desert, this region should be important for the discovery of fungicides, insecticides, and herbicides as well as sources of accumulated secondary compounds.

Sources of fuels.—Although there is currently little interest in using plant chemicals as sources of liquid fuels, the availability and price of petroleum will likely change such that plants may again become attractive sources of liquid fuels (Calvin 1979, Johnson and Hinman 1980, Wang and Huffman 1981, McLaughlin and Hoffmann 1982, Princen 1982, Adams and McChesney 1983, McLaughlin et al. 1983). The non-polar

Products*	Milkweed fluid bed	Gopherweed fixed bed	Gumweed fixed bed
Gases (C <sub>1</sub> -C <sub>3</sub> )	11%	10%	15%
Gasoline	58%	36%	14%
Diesel and fuel oil	22%	42%	60%
Coke and losses	9%	12%	11%

TABLE 1
FUELS FROM MILKWEED, GOPHERWEED, AND GUMWEED

extract from plants can be converted by zeolite type catalysts (Weisz et al. 1979, Haag et al. 1980) directly to liquid fuel hydrocarbons. A comparison of the cracking products obtained from the biocrude of milkweed (Asclepias spp.), gopherweed (Euphorbia lathryis), and gumweed (Grindelia spp.) is shown in Table 1. If the bagasse (extracted residue) is used to generate electricity, McLaughlin et al. (1983) have shown an additional energy yield of the same magnitude as that of the biocrude. Alternatively, the bagasse may be much more valuable for direct use as cattlefeed (Adams et al. 1983a).

Sources of chemicals.—Chemicals from plants generally have a considerably higher value for chemical feedstocks than for use as fuel (Adams and McChesney 1983, Adams et al. 1983a). Therefore, there has been a shift in research interests in the United States toward the production of moderately priced (\$0.30-\$2.00/lb.; \$0.66-\$4.41/kg) chemicals from plants. With this in mind, I would like to discuss some of the near term (5 years) and horizon (20 years) chemical crops from the Chihuahuan Desert.

Natural rubber can be obtained from guayule (Parthenium argentatum), a desert shrub of the Asteraceae from the Chihuahuan Desert (Fig. 2) of northern Mexico and west Texas (Campos-Lopez and Roman-Alemany 1980). Guayule rubber's molecular weight (1.2 × 106) is comparable to that of the rubber tree (Hevea brasiliensis) (Swanson et al. 1979). The United States currently imports approximately 850,000 tons (770,000 MT) of natural Hevea rubber, principally from Southeast Asia (Chemical Economics Handbook 1979). Guayule rubber production in Mexico reached a peak in 1941–1945 with approximately 40,000 tons (36,400 MT) tons being exported from Mexico (Campos-Lopez and Roman-Alemany 1980). The price of natural rubber is currently about \$0.58/lb. (\$1.28/kg) (Wall Street Journal, 22 Nov. 1983).

<sup>\*</sup>Whole plant extracts can be cracked to liquid fuels and apparently give roughly equivalent products. Data on milkweed (Asclepias speciosa) from Wayne Craig, Saskatechewan Research Council; gopherweed (Euphorbia lathyris); and gumweed (Grindelia squarrosa) from Haag et al. (1980); the differences in extraction solvents (hexane, acetone, and methylene chloride, respectively) may account for most of the differences in the products.



Fig. 2. Test plantation of guayule (Parthenium argentatum) west of Fort Stockton, Pecos Co., Texas. This plantation was developed by Firestone Tire and Rubber Co., but is now managed by Texas A&M University.

Guayule rubber production is constrained by several factors (NAS 1977) including: cold and salt tolerance, problems of seedling establishment, lack of uniform yields, and problems of rubber extraction and deresinification as well as utilization of the by-products (resin and bagasse). Guayule is not considered to be cold tolerant because it goes dormant at temperatures below  $15^{\circ}F$  ( $-9^{\circ}C$ ) and can be killed by sustained freezing temperatures (Foster et al. 1980), although the rootstocks may regrow after a frost. Hybridization with cold tolerant mariola (*Parthenium incanum*) could lead to more cold tolerance (E. Rodriguez, pers. comm.).

Guayule is relatively salt tolerant (Foster et al. 1980) but as the salt concentration is increased in irrigated arid land soils, a more salt tolerant variety could find wide application. Salt tolerance has been selected for in tobacco (Nabors et al. 1980) and several other plant species using tissue culture systems (Bressan et al. 1981, Bhaskaran et al. 1983, Handa et al. 1983). The recent development of tissue culture methods for guayule (Staba and Nygaard 1983) offers promise for in vitro selection.

Seedling establishment is difficult in guayule due to the small seed size and competition with weeds (NAS 1977), although guayule appears to be very competitive once the stand is established (NAS 1977). The efficient extraction of rubber from guayule and deresinification continues to be a

problem that is being examined by Firestone Tire and Rubber Co. (Biomass Digest, June 1983; Sept. 1983) and Texas A&M University (Engler 1982). Two other species of Asteraceae that produce natural rubber are rabbitbrush (*Chrysothamnus nauseosus*) (Hall and Goodspeed 1919) and sunflowers (*Helianthus* spp.) (Stipanovic et al. 1980, Stipanovic et al. 1982).

Candelilla is the source of candelilla wax, a product of the Chihuahuan Desert (Campos-Lopez and Roman-Alemany 1980). The wax, currently selling for \$1.90-\$2.10/lb. (\$4.19-\$4.63/kg) (Chem. Mkt. Rptr., 7 Nov. 1983), is extracted by boiling the entire plant in water to which about 8 lbs. (3.6 kg) of sulfuric acid have been added for every 100 lbs. (45 kg) of plant material (Tunnell 1981). The wax floats to the top of the water, is skimmed off, strained and cooked to remove excess moisture (Tunnell 1981, Bennett 1963). The principal sources of candelilla wax in addition to E. antisyphilitica are (E. cerifera) and (Pedilanthus pavonis) (Bennett 1963). Euphorbia antisyphilitica and E. cerifera, however, are indistinguishable based on the published descriptions (Hodge and Sineath 1955). The differences in the wax obtained from the different plant sources are reported to be small and wax from all three species is sold as candelilla wax (McLoud 1970). In this paper only E. antisyphilitica is considered. Candelilla is a perennial that may produce up to 100 stems (Fig. 3), 0.4-1.2 m tall (Tunnell 1981). It is distributed primarily on well-drained limestone in northern Zacatecas, western Nuevo Leon, eastern Durango, Chihuahua, and Coahuila in Mexico and in El Paso, Hudspeth, Presidio, Jeff Davis, Brewster, Terrell and western Val Verde counties in Texas (Tunnell 1981). Candelilla plants normally require 2-5 years to produce wax in commercial quantities and the waxy coat seems to be thicker during drier periods (NAS 1978). Crude methods of field extraction yield about 2% of the plant's fresh weight in wax which has about 10% impurities (Hodge and Sineath 1955). Yields of 3-5% fresh weight (12-15% dry weight) have been obtained under laboratory conditions (NAS 1978).

The most common constituents of plant waxes are long-chain fatty acids and alcohols (Robinson 1975). However, a wide variety of compounds has been found including long-chain hydrocarbons, acids, alcohols, ketones, aldehydes, triterpenes, and steroids (Chemical Technology 1972; Tulloch 1973; Adams et al. 1983a, b). A common factor in this variety of compounds is their solubility in lipid solvents such as ether and chloroform. Wax fatty acids have an even number of carbon atoms and are generally longer ( $C_{24}$ – $C_{36}$ ) than those found in triglycerides. Alcohol chain length is generally in the same range ( $C_{24}$ – $C_{36}$ ) as the fatty acids.

Illman (1979) investigated the composition of commercial candelilla



Fig. 3. Candelilla (Euphorbia antisyphilitica) growing in the Chihuahuan Desert has been the source of a hard wax for many years.

wax by comparing the IR spectra of the wax to that of its methylene chloride soluble resin. In addition, he compared the differential thermal analysis spectrum of the wax with those obtained from the acid, alcohol, and hydrocarbon fractions of the saponified wax. On the basis of his results and work of others, Illman proposed the composition shown in Table 2 for candelilla wax.

The composition of candelilla wax proposed by Illman agrees reasonably well with those of other workers. Chibnall et al. (1934) found 20% resin, 50–60% hydrocarbon, and that the free alcohols plus the hydrolyzed alcohols were about 35–40% of both  $C_{30}$  and  $C_{32}$  and 10–15% of  $C_{28}$  and  $C_{34}$ . The hydrocarbon was found to be almost pure  $C_{31}$  (95%), hentriacontane. Bennett (1963) reported 28–29% esters, 12–14% alcohol, sterols, neutral resins, 50–51% hydrocarbons, 7–9% acids, 0.5–1% moisture, and 0.7% inorganic matter. Campos-Lopez and Roman-Alemany (1980) reported 29% ester of sitosterol, dihydroxymiricinoleic acid and other esters, 45% hydrocarbon (mostly hentriacontane and tritriacontane) and 26% free alcohols, lactones, and other resinuous materials.

The imports of candelilla wax into the United States give a good indication of the production. From 1936-1951 the imports gradually increased from 1.8 million lbs. (816 MT) in 1939 to a maximum of 10.9

Table 2		
THE COMPOSITION OF CANDELILLA WAX AS PROPOSED BY ILLMAN (1	979)	

Compound class	Chemical substances	
42% hydrocarbon	98% alkane (7 components) principally C <sub>29</sub> , C <sub>31</sub> , C <sub>33</sub> 2% 1-alkane (16 components) principally C <sub>28</sub> , C <sub>30</sub> , C <sub>31</sub> , C <sub>32</sub>	
39% ester	C <sub>42</sub> to C <sub>68</sub> (including esters of sitosterol and dihydroxymyricinsaure)	
6% lactone	delta-lactone of dihydroxymyricinsaure	
8% free acid	9% C <sub>28</sub> , 48% C <sub>30</sub> , 43% C <sub>32</sub>	
5% free alcohols	77% C <sub>30</sub> , 20% C <sub>32</sub> , 3% C <sub>34</sub> including 24-methylcycloartenol, lupeol, amyrin, and possibly epi-euphol	

million lbs. (4943 MT) (1943) and stayed at 7-9 million lbs./year (3175-4082 MT) until 1948 (Daugherty et al. 1953). In 1947, the Mexican government prohibited the collection of candelilla and the imports dropped from 8.4 million lbs. (3809 MT) (1947) to 2.6 million lbs. (1179 MT) in 1948 (Daugherty et al. 1953). Imports rebounded to 4-7 million lbs. (181-3175 MT) (1949-1951). Most recently the imports have been decreasing from 871,000 lbs. (395 MT) (1978) to 379,000 lbs. (172 MT) in 1981 (Chemical Economics Handbook 1982). Prices for candelilla wax have ranged from \$0.13 cents/lb. (\$0.29/kg) in 1936 (Tunnell 1981) and upward to today's price of \$1.90-\$2.10/lb. (\$4.18-\$4.63/kg) (Chem. Mkt. Rptr., 7 Nov. 1983).

Two major problems for the domestication of candelilla are stand establishment in the desert and developing harvesting methods that do not kill the plants (Daugherty et al. 1953). Selection for genotypes that can withstand coppicing would seem to offer considerable merit. Candelilla grows vigorously when water is applied but then little wax is produced. If clones are found that can withstand coppicing, a drip irrigation system might be used to grow the the plants and then stress them to induce high wax yields.

Although there is no major federal (U.S.) program to develop candelilla as a cultivated crop, research in Mexico has been on-going for several years (Campos-Lopez and Roman-Alemany 1980) and several ranchers (Duncan Cooper, pers. comm.) and a few scientists are conducting limited field trials in the U.S.

A liquid wax can be obtained from the seeds of jojoba (Simmondsia chinensis, Buxaceae), in approximately 50% yield. Jojoba is native to the Sonoran Desert of northern Mexico and the southwestern United States but it might be introduced into the most frost-free areas of the Chihuahuan

Desert. The oil is composed of long-chain esters that are stable at high temperatures and are potentially useful as lubricants (Hogan 1979). Its major use today is in the cosmetics industry (Haumann 1983). Currently most of the jojoba comes from natural stands. The first commercial harvest of 3-year-old plants in the United States was in 1982 with a yield of 50-64 lbs./acre (56-72 kg/ha) (Haumann 1983). An estimated 27,000 acres (10,935 ha) are in cultivation in the United States (Haumann 1983). Jojoba oil sells for approximately \$7-\$8/lb. (\$15.44-\$17.64/kg) (Chem. Mkt. Rptr., 7 Nov. 1983).

The major problem in growing jojoba in most of the Chihuahuan Desert is the lack of cold tolerance in any of the commercial varieties. Although jojoba can withstand temperatures as high as 110°-122°F (43°-50°C), it appears to be limited by temperatures below 17°F (-8°C) (NAS 1979). Jojoba is also limited by the need to determine the sex of the plants, a lack of proven superior seed sources, the long period needed before the plants achieve full production potential (NAS 1975), and potential competition from synthetic jojoba oil (Haumann 1983).

One way to overcome some of these problems may be through tissue culture of male and female plants of selected germ lines. Native Plants, Inc. (Salt Lake City, Utah) is currently producing commercially available tissue-cultured plants of known gender (Fig. 4). If frost tolerant genotypes were to be discovered, they could be readily multiplied by tissue culture. Jojoba development is actively supported by numerous venture capital groups and various federal research programs (particularly benefiting from the years of research by D. M. Yermanos and T. K. Miwa).

Gums are economic chemicals associated with arid lands in several cases. One of the most important of these is gum arabic which is obtained from Acacia senegal (Fabaceae) which occurs in the arid lands of Africa and the Middle East (NAS 1979). Acacia gum is used in adhesives, bakery products, candies, ice cream, cosmetics, and many foods to suspend solids and emulsify ingredients (NAS 1979). The United States imports approximately 5600 tons (5082 MT) annually (Chem. Mkt. Rptr., Imports, 1981, 1982). This gum currently sells for approximately \$1.15/lb. (\$2.54/ kg) (Chem. Mkt. Rptr., 7 Nov. 1983). Over 100 species of Acacia are known to produce gum. A major center of diversity appears to be in Mexico and some Acacia spp. native to the Chihuahuan Desert might be good candidates for a domestic source of this gum (NAS 1979). However, a chemical that is to be used in food (in the United States) must be obtained from an approved plant source listed in the Food Chemicals Codex (1981) to be regarded as GRAS (generally recognized as safe). Otherwise, a new plant source of a food chemical must be approved by the Food and Drug Administration (FDA). Most companies in the United States are reluctant

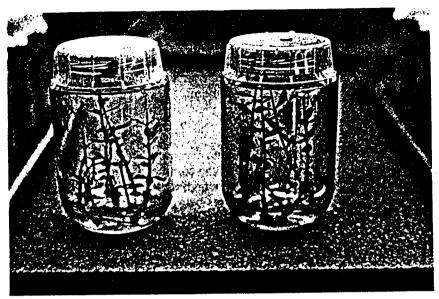


Fig. 4. Tissue cultured plantlets of jojoba (Simmondsia chinensis) being multiplied at Native Plants, Inc., Salt Lake City, Utah.

to develop new crops for food chemicals because of the enormous costs to obtain FDA approval (W. McNabola, pers. comm.). Bearing this in mind, it is illustrative to examine the Food Codex (3rd Ed.) which specifies the source of Arabic (Acacia) gum as "A dried gummy exudation obtained from the stems and branches of Acacia senegal (L.) Willd. or of related species of Acacia (Leguminosae)" (Food Chemicals Codex 1981). Whether Acacia spp. of the New World can come under the "or of related species of Acacia" definition in the Food Codex is not known. Another constraint might be passing the Food Codex test for tannins since many of the acacias may be rich in tannins (see below).

Another important gum (tragacanth) comes from Astragalus gummifer (Fabaceae) and related species. The gum is collected from wild bushes in the arid mountains of Iran, Iraq, and Turkey, as well as Pakistan, Afghanistan, Syria, Israel, and Greece (NAS 1979). Iran has been the major supplier in recent years or was until political upheaval there. The plants are widely scattered in remote, inhospitable semi-deserts, and natural stands are becoming depleted. The exact species which produce the gum, as well as the environmental and genetic factors which control gum production are still virtually unknown. Except for a few test plantings in California (H. Scott Gentry, pers. comm.), the cultivation of gum traga-

canth-producing Astragalus spp. has never been attempted. Limited efforts have shown, however, that the plants can be grown from seed in semi-arid areas similar to those in the highlands of Asia Minor, such as in California, New Mexico, and Arizona between 4000 and 8000 ft (1200–2400 m). Gum tragacanth is used in pharmaceuticals, cosmetics, and as a thickening agent in foods (NAS 1979). Due to the political instability in the area of production, imports are erratic and only approximately 139 tons (126 MT) were imported in 1982 at a price of \$38/lb. (\$83.79/kg) (Chem. Mkt. Rptr., 7 Nov. 1983). No other gum has yet been found that is a complete substitute for tragacanth gum. However, the species might be adapted to the higher, colder regions of the Chihuahuan Desert. Except for a small program by the National Science Foundation (H. Scott Gentry, pers. comm.), there appears to be no other active development program at this time.

Diterpene acids are produced in many species from the Chihuahuan Desert but species in the Asteraceae are particularly rich in these compounds (McLaughlin and Hoffmann 1982, Adams and McChesney 1983). Grindelia spp. and Chrysothamnus spp. are the highest yielding (nonpolar extractables) taxa examined from the southwestern U.S. deserts (McLaughlin and Hoffmann 1982). Of these two genera, Grindelia may offer more promise in the Chihuahuan Desert. Both genera are rich in diterpene acids (Bohlmann et al. 1982, Hoffmann et al. 1982, Timmermann et al. 1983). The diterpene acids from Grindelia spp. might be substituted for the diterpene acids from wood rosins of the naval stores industry. The abietic acid derivatives from pine trees have numerous uses, such as paper sizing, emulsifying and tackifying agents in rubber, adhesives, surface coatings, printing inks, and chewing gum (Zinkel 1975, 1981). The development of members of the Asteraceae as sources of diterpene acids is currently being sponsored by Hercules Inc. and the National Science Foundation at the University of Arizona. The problems encountered in this development are typical for most new crops: cultivation, breeding, disease, harvesting, processing, and marketing. These kinds of chemical crops are probably horizon ventures (20 years).

Soaps (saponins) for shampoos are currently being extracted from various species of Yucca (Agavaceae) (Campos-Lopez and Roman-Alemany 1980). The commercial potential of Yucca is uncertain because their saponins are used in cosmetic soaps and the manufacturers often switch to other plant sources merely to introduce a different advertising campaign.

Antioxidants are common in plants and typical compounds include flavones, isoflavones, flavonols, catechins, eugenol, coumarin compounds, tocopherols, cinnamic acids, phosphatides, and polyfunctional

organic acids (Dugan 1980). Plant flavonoids, particularly flavonols and flavonol glycosides are among the most potent phenolic antioxidants (Pratt 1980). However, the use of polyphenolic flavonoids as antioxidants is problematical since there are possible negative health effects (Pratt 1980, Ames 1983). The major use of antioxidants is in cured rubber to prevent oxidation and ozonolysis where 205 million lbs. (92,968 kg) valued at \$0.85 cents/lb. (\$1.87/kg) were used in 1976 (Nicholas et al. 1978). The second largest use of antioxidants is in plastics where 29.2 million lbs. (13,242 kg) were used in 1976 (Nicholas et al. 1978) and 59.5 million lbs. (35,402 kg) in 1980 (Chemical Economics Handbook 1982). Other uses are in lubricants, adhesives, food, and animal feed. The best known source of antioxidants in the Chihuahuan Desert is the creosote bush (Larrea tridentata, Zygophyllaceae), which is a dominant shrub (Fig. 5) throughout much of the region (Mabry et al. 1977, Campos-Lopez and Roman-Alemany 1980). The principal antioxidant from Larrea is nordihydroguaiaretic acid (NDGA) which was discovered in the resinous exudate of L. divaricata in 1942 (Waller 1942, Waller and Gisvold 1945). NDGA has been reported in yields of 8.9% dry weight from leaves on summer growth (Duisberg 1952) and 5.2% dry weight for leaves of regrowth from stumps. Rhoades (1977) reported 12.5% dry weight yields of catechols (NDGA plus other lignans) in young leaves (folded leaf tips) and 3.82% dry weight in mature leaves. The major source of the antioxidant, NDGA (from 1942 to 1972) was apparently Larrea (Oliveto 1972, Timmermann 1977). However, researchers at the Canadian Food and Drug Directorate reported that rats fed up to 3% NDGA in their diet developed cortical and medullary cysts in the kidneys (Grice et al. 1968, Goodman et al. 1970). These reports resulted in the U.S. Food and Drug Administration removing NDGA from the GRAS list (Oliveto 1972, Timmermann 1977). The development of an efficient method for chemical synthesis of NDGA by Hoffman-LaRoche (Perry et al. 1972) might present serious competition for the revitalization of the usage of NDGA from plants. However, the industrial (non-food) uses of NDGA in rubber, plastic, lubricants, and adhesives should be investigated if NDGA and related compounds were generated as by-products from range improvement projects (J. Nelson, pers. comm.). Other uses of creosote bush include: livestock feed from the extracted residue (Adams 1970), medicines (see references in Timmermann 1977), as a source of natural insect anti-feedants (Rhoades 1977), and for use in phenolic resins (Campos-Lopez and Roman-Alemany 1980).

Tannins are bitter tasting, complex polyphenolic compounds found in most plants but particularly in woody, perennial species (Swain 1979). Tannins appear to offer resistance to herbivores in apparent species by



Fig. 5. Branch of creosote bush (*Larrea tridentata*). Note the lack of any obvious antiherbivore characteristics such as thorns. The leaves contain considerable amounts of bittertasting phenolics that apparently reduce browsing.

complexing with leaf proteins to decrease the available nitrogen from the leaves (Donnelly and Anthony 1969, Feeny 1976, Cates and Rhoades 1977, Rhoades 1977, Lohan and Negi 1981, Schultz et al. 1982, Provenza and Malechek 1983). Commercially, tannins are used for leather tanning, drilling muds, adhesives for composite wood products, cardboard manufacture, ore recovery, and in water purification (Roux et al. 1980). Essentially all the plant tannins used in the United States are imported. The two major sources of plant tannins are: quebracho (Schinopsis spp.) (Anacardiaceae) from Argentina and Paraguay with 15% condensed tannins in the wood (Roux et al. 1980); and wattle (Acacia mernsii [Fabaceae] from Brazil and southern Africa with 35% tannins in the bark. Approximately 30 million lbs. (13,605 kg) of quebracho products and 18.5 million lbs. (8390 kg) of wattle derivatives were imported into the United States in 1976 at about \$0.41 cents/lb. (\$0.90/kg) (U.S. Bureau of the Census 1977). Because Acacia and related genera are abundant in the Chihuahuan Desert, these renewable sources of this imported commodity (tannin) should be investigated. Development of these new sources will involve problems of harvesting and processing as well as competition from foreign suppliers. Currently research is being conducted on Acacia spp. as domestic tannin sources by Dr. David Siegler (pers. comm.) and is sponsored by the National Science Foundation (U.S.).

Biologically active compounds are obtained from many plants. The most familiar plant derived drugs are probably morphine from Papaver somniferum and digitalis from Digitalis purpurea (Tyler et al. 1976). However, because of the co-evolutionary interaction between plants and diseases in the Chihuahuan Desert (see introduction), one should anticipate that biocides of considerable variation have evolved. Campos-Lopez and Roman-Alemany (1980) list several Chihuahuan Desert species with possible pesticide activity: castor bean (Ricinus communis) (insecticides); creosote bush (fungicide); scarlet pimpernel (Anagallis arvensis) (fungicide); jimson-weed (Datura stramonium) (nematodicide); and tree tobacco (Nicotiana glauca) (aphidicide). In addition, they mention numerous species in the genera Agave, Yucca, Acacia, Maguey, and Opuntia that contain compounds with pharmacological activity (table VII, Campos-Lopez and Roman-Alemany 1980). Biologically active compounds from Chihuahuan Desert species might be used directly as precursors for derivatives or as models for structure related activity studies and subsequent drug design.

# DISCUSSION

Some major problems of growing plants in arid lands are that: (1) biomass/area is low and harvesting costs may be expensive; (2) wind and water soil erosion is already severe, and crops will have to be managed very carefully to avoid these problems; and (3) a monoculture of an arid land crop may allow the natural predators to increase (of course, this is a problem in any monoculture).

Although the primary (or initial) emphasis may be on a single chemical (or class of chemicals), very few potential crops examined to date appear to be economically feasible if only a single product is obtained. Because of the cost to grow, harvest, and extract chemicals, it is important to examine each species for multiple uses (Buchanan et al. 1980, Adams 1982, Adams et al. 1983a). After the plant material has been transported to a central processing facility, the cost to extract the material by several methods may not be large, but one can potentially produce considerably more products. For example, candelilla produces a fine wax, but this only accounts for 12–15% (dry weight) of the biomass. Cellulose in the remaining 85–88% can be used in fermentation or the bagasse used for animal feed. In general, non-polar solvent extraction removes chemicals which might be useful as waxes, lubricants, and elastomers. Polar solvents extract compounds that contain reactive oxygen groups. These compounds may be more useful as chemical intermediates since they may

contain highly reactive groups. They may be used as adhesives, coatings, UV absorbers, antioxidants, dyes, etc. The polar fraction is also where one finds the greatest concentration of biologically active compounds (McChesney and Adams 1984).

A water (or acidic aqueous) extraction may yield a gum such as tragacanth or other valuable polysaccharides such as pectin. Some water-soluble protein may be also recovered at this step. The principal products left after these extractions are cellulose, hemi-cellulose, lignin (if present), and protein. This extracted residue can be non-toxic if the biologically active compounds (if present) have been extracted previously. Several possibilities exist for the use of the residue. Some may be burned to generate plant processing power. It may be burned in power generation stations in place of coal (Buchanan et al. 1980, McLaughlin et al. 1983). Fiber may be removed during the processing for use as paper, pulp, or fabric. The extracted residue usually has an enriched concentration of protein, by the ratio of extractables to bagasse, and may be used as a livestock feed. The residue could also be digested by fermentation to produce industrial chemicals (Palsson et al. 1981).

In summary, the aforementioned sources of chemicals should be further studied in regards to products, markets, problems, and potentials for domestic utilization if real chemical products are to be produced from Chihuahuan Desert plants on a sustained basis.

### LITERATURE CITED

- ADAMS, D. W. 1970. A study of the possibilities of treating creosote bush with NaOH to make a good livestock feed. M.A. thesis, Sul Ross State Univ., Alpine, Texas.
- ADAMS, R. P. 1982. Production of liquid fuels and chemical feedstocks from milkweed. Pp. 1113-1128 in Energy from biomass and wastes (D. L. Klass, ed.). Institute of Gas Technology, Chicago, Illinois.
- AND J. D. McChesney. 1983. Phytochemicals for liquid fuels and petrochemical substitutions: extraction procedures and screening results. Econ. Bot. 37:207-215.
- M. F. BALANDRIN, AND J. R. MARTINEAU. 1983a. The showy milkweed, Asclepias speciosa: a potential new semi-arid land crop for energy and chemicals. Biomass 4:81–104.
- —, L. Hogge, W. Craig, and S. Price. 1983b. Analysis of the nonpolar extractables of *Asclepias speciosa*. J. Am. Oil Chem. Soc. 60:1315-1318.
- AMES, B. N. 1983. Dietary carcinogens and anticarcinogens. Science 221:1256-1264.
- BENNETT, H. 1963. Industrial waxes, 2nd Ed. Vol. I. Chemical Publ. Co., New York, New York.
- BHASKARAN, S., R. H. SMITH, AND K. SCHERTZ. 1983. Sodium chloride tolerant callus of Sorghum bicolor (L.) Moench. Z. Pflanzenphysiol. Bd. 112:459-463.
- BOHLMANN, F., M. AHMED, N. BORTHAKUR, M. WALLMEYER, J. JAKUPOVIC, R. M. KING, AND H. ROBINSON. 1982. Diterpenes related to grindelic acid and further constituents from *Grindelia* species. Phytochemistry 21:167-172.
- Bressan, R. A., P. M. Hasegawa, and A. K. Handa. 1981. Resistance of cultured higher plant cells to polyethylene glycol-induced water stress. Plant Sci. Letters 21:23-30.

- BRYANT, J. P. 1981. Phytochemical deterrence of snowshoe hare browsing by adventitious shoots of four Alaskan trees. Science 213:889-890.
- Buchanan, R. A., F. H. Otey, and G. Hamerstrand. 1980. Multiuse botanochemical crops, an economic analysis and feasibility study. Ind. Eng. Chem. Prod. Res. Dev. 19: 489-496.
- CALVIN, M. 1979. Petroleum plantations for fuel and materials. Bioscience 29:533-538. CAMPOS-LOPEZ, E. AND E. ROMAN-ALEMANY. 1980. Organic chemicals from the Chihuahuan Desert. J. Agric. Food Chem. 28:171-183.
- CATES, R. G. AND D. F. RHOADES. 1977. Patterns in the production of antiherbivore chemical defenses in plant communities. Biochem. Syst. Ecol. 5:185-193.
- CHEMICAL ECONOMICS HANDBOOK. 1979. Vol. 6. Marketing research on natural rubber. Pp. 525.2008R-525.2100. Stanford Res. Inst., Menlo Park, California.
- ----. 1982. Vol. 17. Marketing research on waxes. Pp. 595.5020A-595.5022J. Stanford Res. Inst., Menlo Park, California.
- CHEMICAL TECHNOLOGY. 1972. An encyclopedic treatment. Vol. 5. Natural organic materials and related synthetic products. Pp. 19-185 in Waxes. Barnes and Noble Books, New York, New York.
- CHIBNALL, A. C., S. H. PIPER, A. POLLARD, E. F. WILLIAMS, AND P. N. SAHAI. 1934. Constituents of waxes. Biochem. J. 28:2189.
- Daugherty, P. M., H. H. Sineath, and T. A. Wastler. 1953. Industrial raw materials of plant origin III. Survey of candelilla and candelilla wax. Bull. 16, Vol. 15, No. 12, 1-56. Engr. Expt. Sta. of Georgia Inst. of Tech., Atlanta, Georgia.
- Donnelly, E. D. and W. B. Anthony. 1969. Relationship tannin, dry matter digestibility and crude protein in *Sericea lespedeza*. Crop Sci. 9:361-362.
- DUGAN, L. R. 1980. Natural antioxidants. Pp. 261-282 in Antioxidation in food and biological systems (M. G. Simic and M. Karel, eds.). Plenum Press, New York, New York.
- Duisberg, P. C. 1952. Some relationships between xerophytism and the content of resin, nordihydroguaiaretic acid, and protein of *Larrea divaricata* Cav. Plant Physiol. 27: 769-777.
- ENGLER, C. R. 1982. Development of process to extract rubber latex from guayule shrub. Pp. 152-161. in Ann. rept. to the Natural Fiber and Food Protein Commission. Sept. 1, 1981-Aug. 31, 1982. Texas A&M University, College Station, Texas.
- FEENY, P. 1976. Plant apparency and chemical defense. Pp. 1-40 in Biochemical interactions between plants and insects. Recent adv. in phytochem., Vol. 10 (J. W. Wallace and R. L. Mansell, eds.). Plenum Press, New York, New York.
- FOOD CHEMICALS CODEX. 1981. Food and Nutrition Board. Committee on Codex specifications, 3rd Ed. National Academy Press, Washington, D.C.
- FOSTER, K. E., W. G. McGINNES, J. G. TAYLOR, T. L. MILLS, R. R. WILKINSON, F. C. LAWLESS, J. MALONEY, AND R. C. WYATT. 1980. A technology assessment of guayule rubber commercialization. Final Report. Office of Arid Lands Studies, Tucson, Arizona and Midwest Research Inst., Kansas City, Missouri.
- GOODMAN, T., H. GRICE, G. BECKING, AND F. SALEM. 1970. A cystic nephropathy induced by nordihydroguaiaretic acid in the rat. Light and electron microscopic investigations. Lab. Invest. 23:93-107.
- GRICE, H., G. BECKING, AND T. GOODMAN. 1968. Toxic properties of nordihydroguaiaretic acid. Food Cosmet. Toxicol. 6:155-161.
- HAAG, W. O., P. G. RODEWALD, AND P. B. WEISZ. 1980. Catalytic production of aromatics and olefins from plant materials. Symposium on alternative feedstocks for petrochemicals. August 24-25. Am. Chem. Soc. Meeting, Las Vegas, Nevada.

- HALL, H. M. AND T. H. GOODSPEED. 1919. Chrysil, a new rubber from *Chrysothamnus nauseosus*. U. Calif. Publ. Botany 7:183-264.
- HANDA, S., R. A. BRESSAN, A. K. HANDA, N. C. CARPITA, AND P. M. HASEGAWA. 1983. Solutes contributing to osmotic adjustment in cultured plant cells adapted to water stress. Plant Physiol. 73:834-843.
- HAUMANN, B. F. 1983. First harvest of cultivated plantations bringing desert crop closer to widespread commercial use. J. Am. Oil Chem. Soc. 60:45-58.
- HODGE, W. H. AND H. H. SINEATH. 1955. The Mexican candelilla plant and its wax. Econ. Bot. 9:134-154.
- HOFFMANN, J. J., S. P. McLAUGHLIN, S. D. JOLAD, K. H. SCHRAM, M. S. TEMPESTA, AND R. B. BATES. 1982. Constituents of *Chrysothamnus paniculatus* (Compositae): chrysothame, a new diterpene and 6-oxogrindelia acid. J. Org. Chem. 47:1725-1727.
- HOGAN, L. 1979. Jojoba: a new crop for arid regions. Pp. 177-206 in New agricultural crops (G. A. Richie, ed.). Westview Press, Boulder, Colorado.
- ILLMAN, G. 1979. Candelilla wax: recovery, composition and properties. Fette, Siefen, Anstrichmittel. 81(8):322-326.
- JOHNSON, J. D. AND C. W. HINMAN. 1980. Oils and rubber from arid land plants. Science 208:460-464.
- LOHAN, O. P. AND S. S. NEGI. 1981. Fractionation of tannins in oak tree leaves. Indian J. Anim. Sci. 51:1019-1025.
- MABRY, T. J., J. H. HUNZIKER, AND D. R. DIFEO, JR. (EDS.). 1977. Creosote bush, biology and chemistry of *Larrea* in New World deserts. US/IBP Synthesis Series 6. Dowden, Hutchinson and Ross, Inc., Stroudsburg, Pennsylvania.
- McChesney, J. D. and R. P. Adams. 1984. Co-evaluation of plant extracts as petrochemical substitutes and for biologically active compounds. Econ. Bot. 39:74-86.
- McLAUGHLIN, S. P. AND J. J. HOFFMANN. 1982. Survey of biocrude-producing plants from the Southwest. Econ. Bot. 36:323-339.
- ——, B. E. KINGSOLVER, AND J. J. HOFFMANN. 1983. Biocrude production from arid lands. Econ. Bot. 37:150–158.
- McLoud, E. S. 1970. Waxes. Pp. 156-173 in Kirk-Othmer encyclopedia of chemical technology, 2nd Ed. Vol. 22. Wiley Interscience, New York, New York.
- NABORS, M. W., S. E. GIBBS, C. S. BERNSTEIN, AND M. E. MEIS. 1980. NaCl-tolerant tobacco plants from cultured cells. Z. Pflanzenphysiol. Bd. 97:13-17.
- NATIONAL ACADEMY OF SCIENCES. 1975. Underexploited tropical plants with promising economic value. The National Academy of Sciences, Washington, D.C.
- ——. 1977. Guayule: an alternative source of natural rubber. The National Academy of Sciences, Washington, D.C.
- -----. 1978. Underexploited tropical plants with promising economic value. Revised ed. The National Academy of Sciences, Washington, D.C.
- -----. 1979. Tropical legumes: resources for the future. The National Academy of Sciences, Washington, D.C.
- NICHOLAS, P. P., A. M. LUXEDER, L. A. BROOKS, AND P. A. HAMMES. 1978. Antioxidants and antiozonants. Pp. 128-148 in Kirt-Othmed encyclopedia of chemical technology. Vol. 3, 3rd Ed. Wiley Interscience, New York, New York.
- OLIVETO, E. P. 1972. Nordihydroguaiaretic acid, a naturally occurring antioxidant. Chem. and Indust. 17:677-679. (Sept. 2.)
- Palsson, B. O., S. Fathi-Afshar, D. F. Rudd, and E. N. Lightfoot. 1981. Biomass as a source of chemical feedstocks: an economic evaluation. Science 213:513-517.
- Perry, C. W., M. V. Kalnins, and K. H. Deitcher. 1972. Synthesis of lignans. I. Nor-dihydroguaiaretic acid. J. Org. Chem. 37:4371-4376.

- PRATT, D. E. 1980. Natural antioxidants of soybeans and other oil seeds. Pp. 283-293 in Antioxidation in food and biological systems (M. G. Simic and M. Karel, eds.). Plenum Press, New York, New York.
- PRINCEN, L. A. 1982. Alternate industral feedstocks from agriculture. Econ. Bot. 36:302–312.
- PROVENZA, F. D. AND J. C. MALECHEK. 1983. Tannin allocation in blackbrush (Coleogyne ramosissima). Biochem. Syst. Ecol. 11:233-238.
- RADWAN, M. A. AND G. F. CROUCH. 1978. Selected chemical constituents and deer browsing preferences of Douglas fir. J. Chem. Ecol. 4:675-683.
- RHOADES, D. F. 1977. The antiherbivore chemistry of Larrea. Pp. 135-175 in Creosote bush, biology and chemistry of Larrea in New World deserts (T. J. Mabry, J. H. Hunziker, and D. R. DiFeo, Jr., eds.). Dowden, Hutchinson and Ross, Inc., Stroudsburg, Pennsylvania.
- ROBINSON, T. 1975. The organic constituents of higher plants, 3rd Ed., pp. 1-87. Cordus Press, North Amherst, Massachusetts.
- ROESKE, C. N., J. N. SEIBER, L. P. BROWER, AND C. M. MOFFITT. 1976. Milkweed cardenolides and their comparative processing by Monarch butterflies. Pp. 93-167 in Biochemical interaction between plants and insects. Recent adv. in phytochem. Vol. 10.9 (J. W. Wallace and R. L. Mansell, eds.). Plenum Press, New York, New York.
- ROUX, D. G., D. FERREIRA, AND J. J. BOTHA. 1980. Structural considerations in predicting the utilization of tannins. J. Agric. Food Chem. 28:216-222.
- SCHULTZ, J. C., P. J. NOTHNAGLE, AND I. T. BALDWIN. 1982. Seasonal and individual variation in leaf quality of two northern hardwood tree species. Am. J. Bot. 69:753-759.
- SIEGLER, D. 1977. Primary roles for secondary compounds. Biochem. Syst. Ecol. 5:195–199.
- STABA, E. J. AND B. G. NYGAARD. 1983. In vitro culture of guayule. Z. Pflanzenphysiol. Bd. 109:371-378.
- STIPANOVIC, R. D., D. H. O'BRIEN, C. W. ROGERS, AND K. D. HANLON. 1980. Natural rubber from sunflower. J. Agric. Food Chem. 28:1322-1323.
- —, G. J. SEILER, AND C. W. ROGERS. 1982. Natural rubber from sunflower. 2. J. Agric. Food Chem. 30:613-615.
- STUBBLEBINE, W. H. AND J. H. LANGENHEIM. 1977. Effects of *Hymenaea courbaril* leaf resin on the generalist herbivore *Spodoptera exiqua* (beet armyworm). J. Chem. Ecol. 3:633-647.
- Swain, T. 1979. Tannins and lignins. Pp. 657-672 in Herbivores: their interactions with plant secondary metabolites (G. A. Rosenthal and D. H. Janzen, eds.). Academic Press, New York, New York.
- Swanson, C. L., R. A. Buchanan, and F. H. Otey. 1979. Molecular weights of natural rubbers from selected temperate zone plants. J. Polymer Sci. 23:743-748.
- TIMMERMANN, B. N. 1977. Practical uses of Larrea. Pp. 252-256 in Creosote bush, biology and chemistry of Larrea in New World deserts (T. J. Mabry, J. H. Hunziker, and D. R. DiFeo, Jr., eds.). Dowden, Hutchinson and Ross, Inc., Stroudsburg, Pennsylvania.
- ———, D. J. LUZBETAK, J. J. HOFFMANN, S. D. JOLAD, K. H. SCHRAM, R. B. BATE, AND R. E. KLENCH. 1983. Grindelane diterpenoids from Grindelia camporum and Chrysothamnus paniculatus. Phytochemistry 22:523-525.
- Tulloch, A. P. 1973. Comparison of some commercial waxes by gas-liquid chromatography. J. Am. Oil Chem. Soc. 50:367.
- TUNNELL, C. 1981. Wax, men and money. A historical and archaeological study of candelilla wax camps along the Rio Grande border of Texas. Texas Historical Commission, Austin, Texas.

- Tyler, V. E., L. R. Brady, and J. E. Robbers. 1976. Pharmacognosy. 7th Ed. Lea & Ferbiger, Philadelphia, Pennsylvania.
- U.S. BUREAU OF THE CENSUS. 1977. U.S. imports for consumption and general imports. Report FT 246. Annual 1976. U.S. Gov't. Printing Office. Washington, D.C.
- WALLER, C. W. 1942. A phytochemical study of *Larrea divaricata*. Ph.D. diss. Univ. Minnesota, Minneapolis, Minnesota.
- AND O. GISVOLD. 1945. A phytochemical investigation of Larrea divaricata Car. J. Am. Pharm. Assoc. 34:78-81.
- WANG, S. AND J. B. HUFFMAN. 1981. Botanochemicals: supplements to petrochemicals. Econ. Bot. 35:369-382.
- Weisz, P. B., W. O. HAAG, AND P. G. RODEWALD. 1979. Catalytic production of high grade fuel (gasoline) from biomass compounds by shape-selective catalysis. Science 206:57-58.
- ZINKEL, D. F. 1975. Naval stores: silvichemicals from pine. Pp. 309-327 in Applied polymer symposium No. 28 (T. E. Timell, ed.). John Wiley and Sons, New York, New York.
- -----. 1981. Turpentine, rosin and fatty acids from conifers. Pp. 163-187 in Organic chemicals from biomass (I. S. Goldstein, ed.). CRC Press, Boca Raton, Florida.