☘Multipurpose Oil-Bearing Plants Tolerant of Arid or Semiarid Environments

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ABSTRACT

Ninety-six plant species from Arizona were examined for their multipurpose oil-producing potential. Whole-plant samples, excluding roots, were analyzed for "oil," "polyphenol," "hydrocarbon" and apparent protein contents as well as for botanical features. Oil fractions of species that yielded at least 3.0% oil (dry, ash-free plant basis) were analyzed for classes of lipid constituents. After saponification of these oils, contents of free fatty acids and unsaponifiable matter were determined. Rubber from species that yielded at least 0.4% hydrocarbon was analyzed for average molecular weight and molecular weight distribution. *Mortonia scabrella* yielded the most oil (6.6%) and a substantial amount of polyphenol (16.0%). *Lepidium oblongum* gave 5.8% oil and 27.1% protein. *Apodanthera undulata* gave 5.8% oil and 22.4% protein. *Ligustrum japonicum* yielded 5.3% oil and 27.4% polyphenol. *Olea europaea* yielded the most polyphenol (29.4%), and *Sisymbrium irio* contained the most protein (35.0%). Several other species yielded substantial amounts of oil (up to 5.4%) and/or polyphenol (up to 28.7%). Maximum yield of hydrocarbon was 0.9% for *Euphorbia albomarginata.* Analytical data and a preliminary examination of botanical characteristics suggest that at least 10 of the 96 species should be studied further for their industrial potential. Data are discussed with respect to species previously analyzed at this Center.

INTRODUCTION

There is considerable interest in developing new crops to supplement our increasing need for alternative sources of fuels, chemicals and other materials (1-5). Currently, we are analyzing plants chemically and botanically for their potential as multipurpose energy-producing species. Previously we have analyzed 700 plant species in 96 families (6) and have identified those of interest for our continued study. Most species were collected randomly from 15 states, principally from the Midwest. The percentages of species yielding substantial amounts of oils and/or polyphenols were lower for species from the Midwest than for those from semiarid regions. The terms "oils" and "polyphenols" are used to refer to "whole-plant" fractions extracted with acetone and then partitioned between hexane (oil fractions) and aqueous ethanol (polyphenol fractions). Compositions of the relatively polar polyphenol compounds, for example, can be polyphenolics, phlobaphenes and tannins, whereas the oils can consist of wax esters, triglycerides, fatty acids, sterols, fatty alcohols and resins. Both fractions are highly complex and may vary considerably in composition with respect to species. Oil- and polyphenol-bearing plants that can tolerate arid or semiarid environments could become valuable sources of industrial raw materials (3,4) for regions in need of revegetation and economic development. This report discusses our analyses of 96 additional species from Arizona, bringing the total of all species evaluated in this program to 796 in 102 families. Plant samples were analyzed for yields of oils, polyphenols, hydrocarbons and protein. The term "hydrocarbons" refers to fractions extracted from the plant samples with hexane following acetone extractions. Oils of selected species were analyzed for classes of lipid constituents and for contents of free acids (FA) and unsaponifiable matter (UM) after saponification. Hydrocarbon fractions were examined for the presence of *cis*-1,4-polyisoprene (rubber), *trans*-1,4-polyisoprene (gutta) and waxes. The polyisoprenes were analyzed for average molecular weight and molecular weight distribution. Each species was assigned a "crop rating" on a scale of 5 (best) to 17 based on analytical and botanical criteria previously reported (7). Although such numerical ratings are intended to provide guidance for future work, they are not intended to be limiting or absolute. Each characteristic, including botanical features, needs further investigation. Primarily, analytical data of selected species are discussed in this report.

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EXPERIMENTAL PROCEDURES

Plants were collected by Prof. Robert W. Hoshaw, College of Arts and Science, Department of Ecology and Evolutionary Biology, University of Arizona, Tucson, Arizona, and Charles T. Mason Jr., Curator of Herbarium, College of Agriculture, University of Arizona. Plant specimens were collected in Pima, Santa Cruz and Cochise counties in Arizona between October 1982 and October 1983. Herbaceous specimens and small shrubs were collected as mature whole plants, clipped at ground level. Trees and large shrubs were sampled by cutting representative end growths. Voucher specimens of all species were prepared by the collectors and are kept at the USDA Northern Regional Research Center herbarium. Plant samples (about 500-1000 g, dry basis) were allowed to dry in a sheltered area and then ground in a Wiley-type mill equipped with a screen containing 1 mm-diameter holes. Milled samples were analyzed for volatiles, ash and protein. About 50 g of each milled sample was extracted in a Soxhlet apparatus first with acetone and then hexane (48 hr each solvent). Acetone-soluble fractions were partitioned between hexane and aqueous ethanol (87.5% ethanol) to obtain "oil" and "polyphenol," respectively. The fraction obtained from the 48-hr hexane extraction was the "hydrocarbon." Yields of these fractions were determined gravimetrically. Procedures used for extractions, partitioning, analyses and characterizations of the fractions have been reported previously (7-9).

RESULTS AND DISCUSSION

Chemical Analyses and Ratings

Of the 96 Arizona species analyzed, yields ranged from 0.7-6.6% oil (dry, ash-free, plant-sample basis), 1.9-29.4% polyphenol, <0.1-0.9% hydrocarbon and 3.1-35.0% protein (6.25 × % Kjeldahl nitrogen). Twenty-six species contained at least 3% oil, 14 contained at least 4% oil and 12 contained at least 5% oil. Twelve species had at least 15% polyphenol, and six had at least 20%. Only five species yielded at least 0.5% hydrocarbon (maximum, 0.9%). Fourteen species had at least 18% protein, and four had at least 22%. These species, including those from Arizona previously reported, have yielded such amounts of oil, polyphenol and/or protein nearly 2.5 times more frequently than Midwest species analyzed at this Center. However, minimum and maximum yields for species from both regions are similar. Fewer than 1% of the species analyzed from either region yielded more than 2% hydrocarbon.

Table I presents data for species yielding relatively large quantities of oil, polyphenol, hydrocarbon or protein and having ratings of less than 12. Some may be examined in

TABLE I

Analytical Data of Plant Species with Ratings of <12[a]

Family Species Common name	Type of plant	Arizona county[b]	Herbarium voucher number	Oil, %	Polyphenol, %	Hydrocarbon, %	Protein, %	Rating
Anacardiaceae *Rhus lancea* L. f. South African sumac	Shrub	P	80636	3.3	18.1	<0.1	9.6	11
Schinus molle L. Peppertree	Evergreen tree	P	80852	4.7	9.5	<0.1	11.6	10
Caprifoliaceae *Viburnum suspensum* Lindl. Sandankwa viburnum	Evergreen shrub	P	80628	4.8	22.6	0.2	9.0	11
Celastraceae *Mortonia scabrella* Gray Utah mortonia	Evergreen shrub	C	80883	6.6	16.0	0.7	7.5	9
Compositae *Babia absinthifolia* Benth. none	Annual	C	80855	4.8	9.0	<0.1	14.4	10
Encelia farinosa Gray Brittle-bush	Shrub	P	80730	4.4	10.0	<0.1	8.7	11
Hymenoclea salsola Torr. & Gray White burrobush	Shrub	P	80638	3.1	14.8	0.1	18.0	10
Iva ambrosiaefolia (Gray) Gray none	Annual or perennial	C	80884	4.1	10.3	<0.1	14.6	11
Cruciferae *Lepidium oblongum* Small Pepper grass	Annual	P	80857	5.8	3.4	0.3	27.1	11
Ericaceae *Arctostaphylos pungens* HBK. Pointleaf manzanita	Evergreen shrub	P	80675	2.4	23.4	0.5	4.8	10
Leguminosae *Cercidium microphyllum* (Torr.) Rose & Johnson Littleleaf palo verde	Small tree or shrub	P	80742	4.9	11.8	0.2	10.4	11
Oleaceae *Ligustrum japonicum* Thunb. Japanese privet	Evergreen shrub	P	80733	5.3	27.4	0.2	13.6	10
Olea europaea L. Common olive	Tree	P	80745	2.6	29.4	<0.1	7.3	11
Pinaceae *Pinus discolor* Bailey & Hawksw. Nut pine	Evergreen tree	P	80735	4.1	14.9	0.3	6.0	11
Rhamnaceae *Condalia lycioides* (Gray) Weberb. Knifeleaf	Shrub or small tree	P	80746	3.3	5.9	0.5	12.2	10
Rutaceae *Citrus paradisi* Macfad. Grapefruit	Tree	P	80679	1.8	7.9	<0.1	15.2	11
Solanaceae *Solanum elaeagnifolium* Cav. Silverleaf-nettle	Perennial	C	80882	3.1	5.8	<0.1	16.6	11
Ulmaceae *Celtis pallida* Torr. Spiny hackberry	Tree	P	80748	1.9	4.1	<0.1	17.6	11

[a]Yields are on a dry, ash-free sample weight basis.
[b]P = Pima, C = Cochise.

greater detail in a future study. Ten of these species yielded more than 4% oil. *Mortonia scabrella* Gray yielded the most oil (6.6%), a substantial amount of polyphenol (16.0%), less than an average amount of protein (7.5%) and greater than an average amount of hydrocarbon (0.7%). Up to now, few species have yielded such amounts of more than one fraction. The hydrocarbon of this species was predominantly rubber as determined by infrared spectroscopy (8). Weight average molecular weight ($\bar{M}_w$) of the rubber was 168,000, and molecular weight distribution (MWD) was 3.3 as determined by gel permeation chromatography (GPC) (10). The $\bar{M}_w$'s of most plant rubbers are lower than 200,000, and few are higher than 300,000. IR and GPC analyses were not done if hydrocarbon yield was less than 0.4%. *Lepidium oblongum* Small gave the second highest yield of oil (5.8%) and had the highest content of protein. *Olea europaea* L. gave the highest yield of polyphenol (29.4%) but gave moderate to low yields of the three other fractions. *Ligustrum japonicum* Thunb. gave the most oil (5.3%) and polyphenol (27.4%). Also, high oil and poly-

TABLE II

Analytical Data of Plant Species with Ratings of >11[a]

Family Species Common name	Type of plant	Arizona county	Herbarium voucher number	Oil, %	Polyphenol, %	Hydrocarbon, %	Protein, %	Rating
Aristolochiaceae *Aristolochia watsonii* Woot. & Standl. Watson's duchman's pipe	Perennial (herb or shrub)	C	80853	5.4	7.1	0.1	18.8	12
Compositae *Ambrosia confertiflora* DC.[b] Weak-leaved burweed	Perennial	C	80844	2.5	8.7	0.6	12.8	12
Ambrosia deltoidea (Torr.) Payne Triangular bursage	Annual	P	80673	2.2	16.4	<0.1	18.1	13
Cruciferae *Lepidium lasiocarpum* Nutt. Hairy-pod pepper-grass	Annual	C	80856	5.4	5.2	<0.1	12.6	12
Sisymbrium irio L. Desert mustard	Annual	P	80635	2.6	11.2	<0.1	35.0	12
Cucurbitaceae *Apodanthera undulata* Gray Melon-loco	Perennial	C	80881	5.8	6.6	<0.1	22.4	12
Euphorbiaceae *Euphorbia albomarginata* Torr. & Gray Rattlesnake weed	Perennial	C	80860	2.9	6.3	0.9	11.3	13
Gramineae *Schismus arabicus* Nees none	Annual	P	80640	1.4	7.0	<0.1	18.5	14
Leguminosae *Astragalus lentiginosus* Dougl. Specklepod loco	Perennial (or winter annual)	P	80662	1.1	7.4	<0.1	19.3	12
Mimosa biuncifera Benth. Wait-a-minute	Shrub	P	80744	1.5	28.7	<0.1	11.7	12
Malvaceae *Malva parviflora* L. Little mallow	Annual	P	80664	1.5	6.7	<0.1	20.5	13
Solanaceae *Chamasaracha coronopus* (Dunal) Gray Small groundcherry	Perennial	C	80848	2.0	11.8	<0.1	19.9	12
Umbelliferae *Bowlesia incana* Ruiz & Pavon Hairy bowlesia	Annual	P	80630	2.5	11.8	<0.1	28.4	14
Violaceae *Viola odorata* L. English violet	Perennial	P	80633	1.5	6.5	<0.1	19.3	15
Zygophyllaceae *Kallstroemia hirsutissima* Vail Hairy caltrop	Annual	C	80874	1.6	3.9	<0.1	18.3	15
Tribulus terrestris L. Puncture vine	Annual	C	80875	1.9	4.6	<0.1	19.0	15

[a]See footnotes a and b to Table I.

[b]Also *Franseria confertiflora* (DC.) Rydb.

phenol yields were obtained from *Viburnum suspensum* Lindl. (4.8% oil and 22.6% polyphenol) and from *Arctostaphylos pungens* HBK. (2.4% oil + 23.4% polyphenol). *Schinus molle* L., *Bahia absinthifolia* Benth., *Encelia farinosa* Gray, *Iva ambrosiaefolia* (Gray) Gray, *Cercidium microphyllum* (Torr.) Rose & Johnson and *Pinus discolor* Bailey & Hawksw. all are noteworthy with respect to yields of oil (4.1-4.9%). Four other species contained noteworthy amounts of protein (14.6-18.0%).

Table II presents data for selected species, containing noteworthy amounts of oil, polyphenol, hydrocarbon and/or protein, with ratings of 12 or higher. Yields of oil and protein were substantial for *Apodanthera undulata* Gray (5.8% oil and 22.4% protein) and *Aristolochia watsonii* Woot & Standl. (5.4% oil and 18.8% protein). *Lepidium lasiocarpum* Nutt. had 5.4% oil and 12.6% protein. These three species yielded relatively low amounts of polyphenol (5.2-7.1%) and hydrocarbon (0.1% or less). *Mimosa biuncifera* Benth. gave a high yield of polyphenol (28.7%). Twelve of these 16 species contained more than 18% protein. *Sisymbrium irio* L. contained an unusually high amount of protein (35.0%) followed by *Bowlesia incana* Ruiz & Pavon (28.4%). Although *Euphorbia albomarginata* Torr. & Gray yielded the most hydrocarbon (9.9%), this fraction was primarily waxy materials rather than polyisoprene. *Ambrosia confertiflora* DC. yielded 0.6% hydrocarbon, which was primarily rubber with an $\bar{M}_w$ of 41,600 and an MWD of 2.0. Significance of MWD values and uses for low molecular-weight rubber have been discussed previously (10).

TABLE III
Classes of Plant Oil Lipids[a]

Species	Sterols	Other free alcohols	Free fatty acids	Esters		Hydrocarbon
				Triglycerides	Nonglycerides	
Apodanthera undulata	A	A	A	A[b]	A	A[c]
Aristolochia watsonii	A	A	A	A	NA	NA
Bahia absinthifolia	A	A	A	NA	A	NA
Cercidium microphyllum	A	A	A	NA	A	A[c]
Condalia lycioides	A	A	A	NA	A	A[c]
Encelia farinosa	A	A	A	A	A	A[c]
Hymenoclea salsola	A	A	A	NA	A	A[b]
Iva ambrosiaefolia[d]	A	A	A	A[d]	A	NA
Lepidium lasiocarpum	A	A	A	A[b]	A[e]	A[c]
Lepidium oblongum	A	A	A	A[b]	A[e]	NA
Ligustrum japonicum	A	A	A	A	A	A[c]
Mortonia scabrella	A	A	A	A	A	A[c]
Pinus discolor	A	A	A	A	A	NA
Rhus lancea	A	A	A	A	A	A[c]
Schinus molle	A	A	A	A	A	A[b]
Solanum elaeagnifolium	A	A	A	A	A	A[b]
Viburnum suspensum	A	A	A	A	A	A[e]

[a]Classes were indicated by thin layer chromatography. A = apparent (TLC spot found near standard, reference compound). NA = not apparent (no TLC spot apparent).
[b]Light TLC spot compared to standard reference compound.
[c]Trace.
[d]Also a TLC spot found for possible triterpenols.
[e]Heavy TLC spot.

Oil Lipids

Thin layer chromatography (TLC) procedures (7-9) were used to identify classes of oil constituents for species yielding at least 3.0% oil. R_f values of oil constituents before and after saponification were compared to those of a standard mixture of sitosterol, oleyl alcohol, oleic acid, triolein, oleyl laurate and squalene, spotted alongside each oil. Table III shows that oils of all 17 species listed contained sterols, other free alcohols less polar than sterols, free fatty acids and esters. All oils but one contained little hydrocarbon (8). *Viburnum suspensum* oil had a heavy TLC spot for hydrocarbon (squalene reference). Twelve of the 17 oils showed spots for both triglyceride and nonglyceride esters. *Lepidium lasiocarpum* and *Ligustrum oblongum* oils had heavy spots for triglyceride esters and light spots for nonglyceride esters. *Iva ambrosiaefolia* oil probably also contained triterpenols (9). *Bahia absinthifolia, Cercidium microphyllum, Condalia lycioides* and *Hymenoclea salsola* had spots only for nonglyceride esters, but *Aristolochia watsonii* had a spot only for triglyceride esters.

TABLE IV

Oil Saponification Data

Species	Saponified oil fractions	
	Unsaponifiable matter, %	Free acids, %
Apodanthera undulata	6.8	61.3
Aristolochia watsonii	24.4	65.2
Bahia absinthifolia	53.0	47.2
Cercidium microphyllum	52.9	34.6
Condalia lycioides	35.9	46.9
Encelia farinosa	32.5	58.3
Hymenoclea salsola	40.7	43.9
Iva ambrosiaefolia	23.8	38.1
Lepidium lasiocarpum	2.3	77.0
Lepidium oblongum	3.6	49.0
Ligustrum japonicum	38.1	43.0
Mortonia scabrella	53.1	36.0
Pinus discolor	16.3	61.9
Rhus lancea	49.3	41.9
Schinus molle	52.5	39.0
Solanum elaeagnifolium	12.8	66.5
Viburnum suspensum	72.2	22.5

Oil Saponification

Oils of species with 3% or more oil were saponified by conventional procedures (8). Table IV shows amounts of unsaponifiable matter (UM) and total free acids (FA) after saponification. Of the 17 oils listed, three had 2.3-6.8% UM (49-77% FA), four had 12.8-24.4% UM (38.1-66.5% FA), four had 32.5-40.7 UM (43.0-58.3% FA), five had 49.3-53.1% UM (36.0-47.2% FA) and one had 72.2% UM (22.5% FA). Most plant oils analyzed at this Center had about 40-60% UM, while few had such amounts as either *Viburnum suspensum* oil (72.2%) or *Lepidium lasiocarpum* (2.3%). Generally, the combined percentages of UM + FA are about 70-90% of the oil. Amounts of UM + FA were 68-100% for 16 of the 17 oils, whereas the amount was only 52.6% for *Ligustrum oblongum* oil. The lower values resulted from a loss of water soluble and volatile materials during partitioning and drying.

ACKNOWLEDGMENTS

Irene M. Cull and Charles T. Mason provided botanical information, Charles L. Swanson did GPC analysis and Dale W. Ehmke provided some extraction data.

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[Received December 12, 1984]