

# Whole-Plant Oils, Potential New Industrial Raw Materials<sup>1</sup>

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## ABSTRACT

In an extensive screening program, 14 plant species have been identified which have good potential as hydrocarbon- and rubber-producing crops. These plants contain from 5 to 10% oil plus polymeric hydrocarbon on a dry weight basis. Since their dry matter yield should be 11,200 to 22,400 kg/ha/year, they would produce several times as much oil as conventional oilseed crops. In these plants, the oil is not concentrated in storage organs, i.e., seed or fruit tissue, but is distributed throughout the whole plant. Several species are lactiferous, with oil as a major component of the latex. A few which are of primary interest as potential new sources of natural rubber produce an equal yield of by-product oil. A prominent feature of most whole-plant oils is their large component of nonglyceride esters. Such oils could become valuable new feedstocks for production of plasticizers for rubber and plastics and new sources of waxes, long chain alcohols, sterols, terpenes, fatty acids, and other products. A petroleum refinery could be operated on whole-plant oils, and some species are being referred to as potential "gasoline trees."

## INTRODUCTION

Many green plants contain, on a dry weight basis, more than 5% oil plus hydrocarbon that is not concentrated in storage organs. In these plants, oils and hydrocarbons are distributed throughout major plant tissues often as the major component of a latex. Several species are capable of producing up to 22,400 kg/ha/year of dry matter and thus are potentially several times as productive as conventional oilseed crops (1,2). Although there has been little past interest in processing whole plants for oil, there is now great interest in these new and renewable sources of hydrocarbons for energy and raw material uses. Various plant species are being regarded as potential "gasoline trees" (3), as possible domestic sources of natural rubber (4,5) and plastics (6), as new sources of industrial feedstocks, or even just as potential fuels (7). Crop production of whole-plant oils would have to focus on the value of the whole plant. If the whole plant were harvested and utilized (a practical requirement for Guayule rubber, for example), agricultural oil and hydrocarbon production would be compatible with increased food and fiber production. Multi-use crops could be developed to provide fiber, protein, and carbohydrates in addition to high yields of oil and hydrocarbon; they appear to actually offer greatly improved overall agricultural productivity (1,2). Thus, an investment in research is worthwhile for development of such new crops and appropriate high-technology processing. An extensive screening program is underway to identify those species most suited for crop production (1,2).

In this paper we report on the composition of oils from 14 species that have been given favorable crop ratings. One, Guayule (*Parthenium argentatum*), is of much current interest as a source of natural rubber (4). Another, Mole or Gopher Plant (*Euphorbia Lathyris*), has been presented as a potential "gasoline tree" (3). The other 12 species currently attract less attention, but they are productive species

adapted to growth in areas unsuited to Guayule or some "gasoline trees."

## EXPERIMENTAL PROCEDURES

### Plant Materials

The Gopher Plant and Guayule samples were provided from cultivated plots in California (see Acknowledgments). The other plants were collected from the wild in central Illinois. Sassafras (*Sassafras albidum*, a tree) samples consisted of new aerial growth with leaves. The other herbaceous or small woody plant samples consisted of the entire above-ground growth. Plant samples were air dried and stored in a cool dark place, then fine ground prior to extraction as previously described (1).

### Extraction and Fractionation

Lipid materials were exhaustively extracted from air-dried, fine-ground samples by organic solvents with Soxhlet extractors. Whole-plant oils were ordinarily prepared by the previously described partitioning scheme (1,2), although several alternative procedures gave the same results as discussed in the following section.

### Hydrocarbon Characterization

Infrared spectroscopy was used to assess hydrocarbon fractions as to polyisoprene and wax contents (1). Molecular weight distributions and fine structure of the polyisoprenes were determined by gel permeation chromatography and carbon-13 nuclear magnetic resonance spectroscopy, respectively, and have been previously reported (6,8).

### Examination of Oils

Green pigments and polar materials were removed from whole-plant oils by dissolving the crude oil in a suspension of 1 g Darco S-51 activated carbon, 1 g Cellite, and 200 cc hexane per 1 g of oil. After refluxing over steam for 10 min, the suspension was filtered and the filtrate was concentrated in vacuo. Recovery was usually 80-90% of the crude oil; refined oils were clear and straw to orange colored.

The refined oils were saponified and separated into unsaponifiable matter and free acids by usual procedures (9). Then a semi-quantitative estimation of their composition was obtained by means of thin layer chromatography (TLC) and densitometry (10). Side-by-side TLC comparison of standards, oil and its unsaponifiable matter made it easy to infer relative amounts of various lipid classes.

The mixed standards were solutions containing respectively, 0.5% wt/vol, 0.25%, and 0.125% of each sitosterol, oleyl alcohol, oleic acid, triolein, oleyl laurate, and squalene. These mixed standard solutions were applied to TLC plates with 5- $\mu$ l pipettes (150  $\mu$ g, 75  $\mu$ g, and 37.5  $\mu$ g total, respectively). Oil and unsaponifiable matter samples were applied as 2% wt/vol hexane solutions with 5- $\mu$ l pipettes (100  $\mu$ g). Commercial analytical TLC plates, with a 0.25-mm coating of silica gel 60 F-254, from EM Laboratories were used. The developing solvent mixture was 80 parts hexane, 20 parts diethyl ether, and 1 part acetic acid. Detection was by spraying with aqueous 40% H<sub>2</sub>SO<sub>4</sub>-5% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, then charring in an oven at 200 C for 5 min.

TLC plates were scanned with a Schoeffel spectro-

<sup>1</sup>Presented at the AOCS Meeting, St. Louis, May 1978.

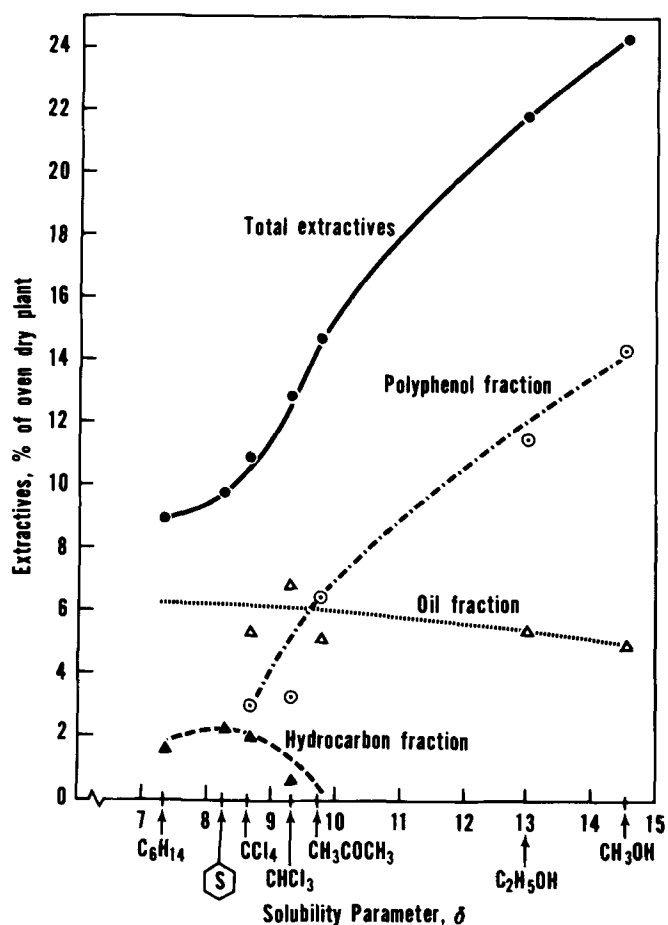


FIG. 1. Extraction of *Asclepias syriaca* with various organic solvents. Solubility parameter ( $\delta$ ) as originally defined by Hildebrand and Scott (11).

densitometer equipped with a recorder to provide plots of light absorbance as a function of migration distance. Concentrations of the various lipid classes in unknown were calculated by comparison of their peak areas to those of the appropriate standard material (10).

## RESULTS AND DISCUSSION

### Whole-Plant Oil Extraction

The quantity and composition of extractives from a given plant depend on the extraction solvent (Fig. 1). Solvents with a solubility parameter ( $\delta$ ) above 9.7 extract a broad range of complex substances but do not extract polymeric hydrocarbons and hard waxes. Solvent with  $\delta$  below about 8.2 extract little of the more polar components ("polyphenol fraction"), but do extract hydrocarbon polymers ("hydrocarbon fraction"). Any of the organic solvents extracted all or nearly all of the nonpolymeric neutral lipids, which we designate "oil-fractions" or "whole-plant oils." Such whole-plant oils are the materials of interest here; they are usually much more complex than plant oils or fats from seed or fruit storage tissue.

As can be deduced from Figure 1, several alternative extraction-partitioning schemes can be employed to prepare equivalent whole-plant oils. A modification of the classic sequential acetone-benzene extraction scheme is used in our laboratory for routine screening and preparation of oil samples (Fig. 2).

### Composition of Select Plants

The overall composition of 14 productive plants species is shown (Table I). In their natural habitat, these are all

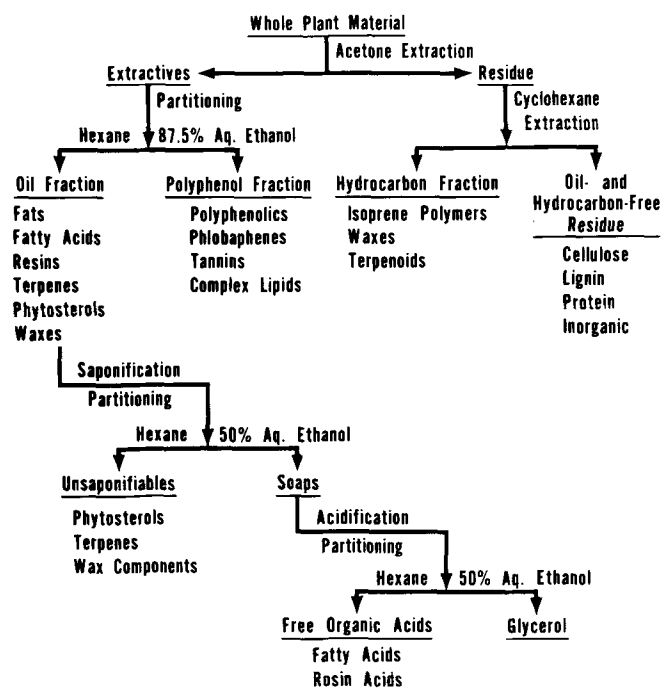


FIG. 2. Scheme for partitioning whole-plant samples and for preparation of whole-plant oils.

vigorously growing, competitive species high in oils and hydrocarbons. Seven species (*Asclepias incarnata*, *A. syriaca*, *Campanula americana*, *Euphorbia dentata*, *E. Lathyrus*, *Rhus glabra*, and *Sonchus arvensis*) are lactiferous with ducts allowing oil and hydrocarbon rich latex to flow at fresh cut surfaces of living plants. Guayule, and probably the remaining Compositae of Table I (*Ambrosia trifida*, *Cacalia atriplicifolia*, *Cirsium discolor*, *Eupatorium altissimum*, and *Vernonia* spp.), contains latex as a cell sap but does not have a vessel system for latex flow. In Guayule the latex is contained in single thin-walled cells (4). Sassafras probably does not contain latex in any form. *Vernonia altissima* is included in Table I because of its close relationship with *Vernonia fasciculata*, with which it hybridizes naturally.

Within a given species, concentration of whole-plant oil changes as the plant matures due to interacting physiological changes. On the whole-plant basis, plants like *Euphorbia dentata* increase in oil as the rather heavy seed matures. However, most wild plants have a low seed weight, and there is little contribution to total oil content. Common milkweed (*Asclepias syriaca*) and some other species shed leaves as their seed matures so that oil content does not increase much but does change in composition. In Sassafras, oil content seems to increase with maturity of new growth wood or perhaps as bark content increases. Other variations probably occur due to the influence of growing conditions, soil fertility, disease, and insect infestation.

### Saponification Yields

Upon saponification of whole-plant oils, the combined yield of unsaponifiable matter and free acids is usually more than 90 parts/100 parts oil (Table II). However, Guayule oil is high in volatile hydrocarbons that escape during analytical manipulations and cause spuriously low unsaponifiable yields and difficult replication of results.

Because the seed oils consist almost entirely of triglycerides, for some species the yield of fatty acids is greatest for samples collected with mature seed, particularly *Asclepias incarnata* 9/23, *A. syriaca* 9/9, *Campanula americana*

TABLE I  
Productive Plant Species

Genus-species	Family	Common name	Harvest date <sup>a</sup>	Crop rating <sup>b</sup>	Crude protein, c %	Polyphenol fraction, c %	Oil fraction, c %	% <sup>c</sup>	Polymeric hydrocarbon Typed
<i>Ambrosia trifida</i> L.	Compositae	Giant ragweed	9/20/77	10	8.8	3.1	4.21	0.40	NR
<i>Asclepias incarnata</i> L.	Asclepiadaceae	Swamp milkweed	10/7/75 7/28/77	10	10.5	4.1	7.60	0.55	NR
<i>Asclepias syriaca</i> L.	Asclepiadaceae	Common milkweed	9/23/75 7/27/77	9	6.5	6.5	4.71	0.67	NR
			8/11/77		10.2	10.3	4.46	1.25	
			9/9/75		---	5.7	4.96	1.64	
			9/30/76		11.1	7.1	4.28	1.39	
			10/23/75		9.8	6.4	5.05	1.26	
			10/26/76		11.3	8.5	3.28	1.09	
<i>Cacalia atriplicifolia</i> L.	Compositae	Pale Indian plantain	8/3/77	8	10.6	5.3	5.74	1.94	NR
<i>Campanula americana</i>	Campanulaceae	Tall bellflower	9/10/76 5/23/77	10	10.6	8.5	3.06	3.10	NR & wax
			9/8/77		15.1	2.6	1.52	0.54	
			9/28/76		8.0	4.2	6.51	1.22	
<i>Cirsium discolor</i> (Muhl.) Spreng.	Compositae	Field thistle	9/28/76	10	9.1	5.8	6.07	0.93	NR & wax
<i>Eupatorium altissimum</i> L.	Compositae	Tall boneset	10/5/77	10	5.3	3.5	5.24	0.36	NR & wax
			9/20/77		8.9	4.0	5.66	0.43	NR & wax
			9/23/75		9.6	9.3	6.08	0.44	NR & wax
			9/29/77		8.0	7.9	5.21	0.35	
<i>Euphorbia dentata</i> Michx.	Euphorbiaceae		7/10/77	10	8.4	9.8	6.17	0.38	NR & wax
			8/25/77		22.1	3.9	2.19	0.23	
			9/28/76		15.2	5.8	4.13	0.31	
<i>Euphorbia Lathyris</i> L.	Euphorbiaceae	Mole plant	3/25/77	10	16.7	3.5	9.68	0.17	NR & wax
<i>Parthenium argentatum</i> A. Gray <sup>e</sup>	Compositae	Gauyule	5/13/77	8	11.8	7.1	9.21	0.37	NR
<i>Rhus glabra</i> L.	Anacardiaceae	Smooth sumac	8/18/77	10	16.6	7.1	4.04	4.58	Wax
<i>Sassafras albidum</i> (Nutt.) Nees	Lauraceae	Sassafras	9/23/75 5/23/77	10	7.6	24.7	5.10	0.31	Wax
			6/29/76		6.6	18.8	5.51	0.20	Wax
			9/8/77		15.3	3.5	2.01	0.20	
			9/10/76		8.8	12.8	3.51	0.10	
<i>Sonchus arvensis</i> L.	Compositae	Sow thistle	6/10/77	10	4.5	6.9	2.26	0.30	NR & wax
<i>Vernonia altissima</i> Nutt.	Compositae	Ironweed	9/9/75	---	8.6	13.9	5.55	0.22	NR & wax
<i>Vernonia fasciculata</i> Michx.	Compositae	Ironweed	5/23/77	10	10.8	3.9	4.63	0.47	NR & wax
			9/6/76		9.3	11.0	5.32	0.72	NR & wax
					18.5	5.9	2.62	0.33	NR & wax
					10.5	7.7	5.01	0.36	NR & wax

<sup>a</sup>Whole plants were harvested and analyzed; generally plants with mature seed had higher oil contents.

<sup>b</sup>Rated on a scale of 5 to 17 where an ideal productive crop species would rate 5 and an impractical species 17. Species scoring 11 or less are possibilities, those scoring 8 or below are of definite crop interest.

<sup>c</sup>All analytical values are on an oven-dry whole-plant basis.

<sup>d</sup>NR = natural rubber *cis*-1,4-polyisoprene identified by IR spectroscopy.

<sup>e</sup>The analysis given is for a 1-year-old shrub; older plants can contain as much as 20% rubber.

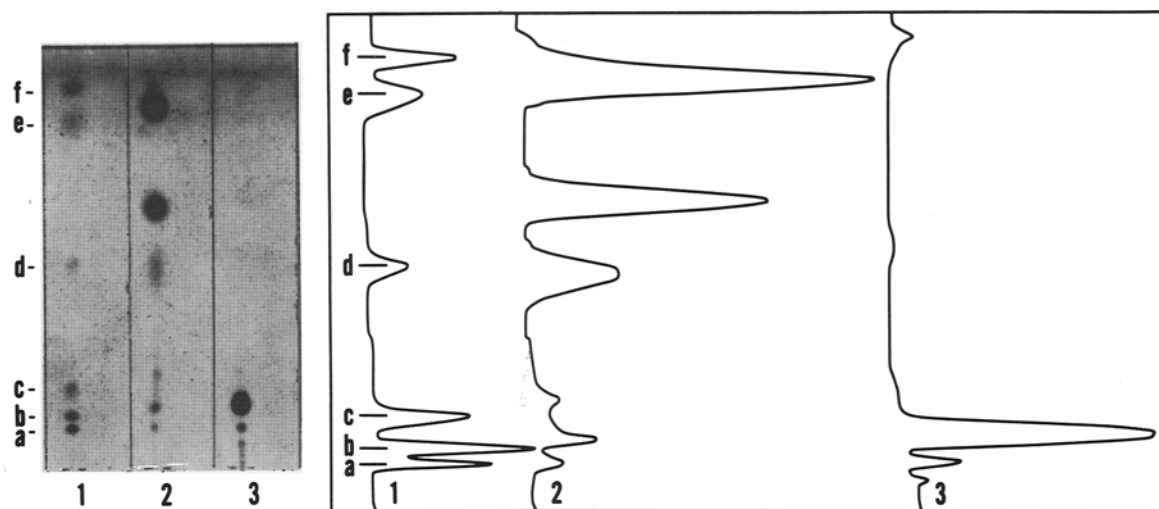


FIG. 3. Thin layer chromatography of a representative whole-plant oil. Lane 1; mixed standard containing (a) sitosterol, RF 0.09, (b) oleyl alcohol, RF 0.12; (c) oleic acid, RF 0.18; (d) triolein, RF 0.47; (e) oleyl laurate, RF 0.80; and (f) squalene, RF 0.87. Lane 2; *Cirsium discolor* oil. Lane 3; *Cirsium discolor* unsaponifiable matter. The densitometer traces are for the corresponding TLC lanes with migration distance expanded 1.25 times.

9/8, and *Euphorbia dentata* 9/28 (Table II). In practice, seed would probably be separated from other plant materials and processed separately. Milkweed seed, for example, has been processed on a pilot scale and gave a good quality oil (12,13).

#### TLC Characterization

TLC comparison of whole-plant oils and their unsaponifiables with standards afforded semi-quantitative measurement of lipid classes (Fig. 3). For example, the yield of free lipid alcohol upon saponification of oils from *Cirsium discolor* and several other plants indicates that the lipids at RF  $\sim 0.6$  and RF  $\sim 0.8$  are nonglyceride esters (Fig. 3). The lipid at RF  $\sim 0.8$  has about the RF of oleyl laurate, a wax ester; the other lipid at RF  $\sim 0.6$  is possibly a triterpenol ester. In the unsaponifiable matter from most whole-plant oils, there were only three TLC fractions corresponding to sterols, other less polar free alcohols and hydrocarbons, respectively (Table II; Fig. 3).

A distinctive feature of most whole-plant oils is their high content of nonglyceride esters less polar than triglycerides (Table III). Eight of fourteen oils had two prominent nonglyceride ester TLC fractions at RF  $\sim 0.6$  and RF  $\sim 0.8$ , probably corresponding to triterpenol and wax esters, respectively. The fraction at RF  $\sim 0.6$  represented from 10 to 40% of the total oil. Triglyceride content, from a trace up to 68%, of whole-plant oils varied inversely with nonglyceride ester content.

All the oils contained hydrocarbons even though much of the volatile terpene content was lost during solvent removal steps in their preparation. For rubber-bearing species, part of the hydrocarbon was probably acetone soluble low-molecular-weight polyisoprene. However, sassafras did not synthesize high-molecular-weight polyisoprene, yet gave an oil rich in hydrocarbons. Guayule oil is rich in terpene hydrocarbons (4).

In sassafras and *Cacalia atriplicifolia* oils and unsaponifiables, there was a prominent TLC fraction of RF  $\sim 0.23$  which was included as free alcohol even though it was considerably less polar than characteristic wax alcohols.

#### Utility of Whole-Plant Oils

Although whole-plant oils from edible plant species have to be considered a potential source of food products, oils from most of the above species are of main interest as

industrial raw materials. Depending on species chosen for crop production and the processing technology employed, a wide variety of chemical intermediates including sterols, long chain alcohols, rosin and fatty acids, esters, waxes, terpenes, and other hydrocarbons could be produced. A substantial market probably exists for crude or slightly refined oils rich in nonglyceride esters as extender oils and/or processing aids for rubber and as plasticizers for plastics. Some whole-plant oils are possibly directly useful in wax and polish formulations. A wide range of petrochemical products as well as the whole range of tall oil, naval stores, and inedible fat products is encompassed. Moreover, if whole-plant oils can be produced at prices competitive with future petroleum prices as seems likely, essentially unlimited markets exist for them as fuels and basic raw materials.

Even if crops are never grown specifically as sources of whole-plant oils, some will very probably be marketed as co- or by-products from production of natural rubber. Large-scale production of whole-plant oils is also highly compatible with the various biomass energy schemes now being proposed.

#### Toxicology Note

*Euphorbia Lathyris*, as well as several other Euphorbiaceae, contains toxic, irritant, and co-carcinogenic esters (14). It is not known whether *Euphorbia dentata* contains these compounds or not. Oils from irritant Euphorbiaceae are reputed to be easily detoxified by alkali-refining, but we are not aware of supporting toxicology data.

Enthusiasts for eating wild plants claim milkweed shoots and buds (*Asclepias syriaca* and possibly *A. incarnata*) and whole young sow thistle plants (*Sonchus arvensis*) are delicious when properly cooked. Tea from sassafras root and bark has been widely enjoyed, and "lemonade" from smooth sumac seed (*Rhus glabra*) is sometimes used. However, we suggest caution in preparation or testing of food, cosmetic, or personal-use products from oils of any of the plants discussed above unless toxicity studies are made.

#### ACKNOWLEDGMENTS

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TABLE II  
Saponification of Whole-Plant Oils

Plant source	Harvest date	Oil content, %	Unsaponifiable yield, g/100 g oil	Acid yield g/100 g oil	Composition of unsaponifiable, estimated by TLC <sup>a</sup>		
					Sterols, %	Other higher alcohols, %	Hydrocarbons, %
<i>Ambrosia trifida</i>	9/20/77	4.21	13.1	80.2	24	43	33
	10/7/75	7.60	8.9	84.0			
<i>Asclepias incarnata</i>	7/28/77	2.70	60.8	35.4	28	64	8
	9/23/75	4.71	25.2	66.1			
<i>Asclepias syriaca</i>	7/27/77	4.46	67.6	24.3	18	78	4
	9/9/75	4.28	39.4	54.0			
<i>Cacalia atriplicifolia</i>	8/3/77	2.99	67.9	26.1	20	60	20
<i>Campanula americana</i>	9/8/77	6.51	15.5	73.8	15	30	55
	9/28/76	6.07	42.5	44.0			
<i>Cirsium discolor</i>	9/28/76	5.24	61.1	32.2			
	10/5/77	5.66	56.1	38.5	12	84	4
<i>Eupatorium altissimum</i>	9/20/77	6.08	39.2	52.7	15	73	12
	9/23/75	5.21	42.6	49.9			
<i>Euphorbia dentata</i>	8/25/77	4.13	42.6	51.8	15	62	23
	9/28/76	9.68	15.9	70.7			
<i>Euphorbia Lathyris</i>	3/25/77	9.21	58.6	30.9	11	80	9
<i>Parthenium argentatum</i>	5/13/77	4.04	46.6	30.2	23	50	27
<i>Rhus glabra</i>	8/18/77	5.10	63.5	27.8	12	80	8
	9/23/75	5.51	55.4	38.3			
<i>Sassafras albidium</i>	9/8/77	2.26	80.2	16.7	14	73	13
	9/10/76	5.55	73.5	19.1			
<i>Sonchus arvensis</i>	6/10/77	4.63	70.7	26.2	15	76	9
	9/9/75	5.32	59.6	32.0			
<i>Vernonia altissima</i>	5/23/77	2.62	64.6	26.9	20	78	2
<i>Vernonia fasciculata</i>	9/6/76	5.01	54.2	38.0			

<sup>a</sup>See Figure 3 for standard materials and R.F. values.

TABLE III  
Lipid Classes in Whole-Plant Oils, Estimated by Thin Layer Chromatography

Plant source	Harvest date	Oil content, %	Oil composition					
			Sterols, %	Other free alcohols, %	Free acids, %	Triglycerides, %	Nonglyceride esters, %	Hydrocarbons, %
<i>Ambrosia trifida</i>	9/20/77	4.21	11	4	7	68	7	3
<i>Asclepias incarnata</i>	7/28/77	2.70	9	15	8	13	48 <sup>a</sup>	7
<i>Asclepias syriaca</i>	7/27/77	4.46	5	11	5	trace	72 <sup>a</sup>	7
<i>Cacalia atriplicifolia</i>	8/3/77	2.99	10	24 <sup>b</sup>	7	10	43	6
<i>Campanula americana</i>	9/8/77	6.51	13	5	10	58	10	4
<i>Cirsium discolor</i>	10/5/77	5.66	2	4	4	21	67 <sup>a</sup>	2
<i>Eupatorium altissima</i>	9/20/77	6.08	6	5	7	36	44 <sup>a</sup>	2
<i>Euphorbia dentata</i>	8/25/77	4.13	6	6	5	42	36 <sup>a</sup>	5
<i>Euphorbia Lathyrus</i>	3/25/77	9.21	3	20	18	3 <sup>c</sup>	49	7
<i>Parthenium argentatum</i>	5/13/77	4.04	10	7	5	23	31 <sup>a</sup>	24
<i>Rhus glabra</i>	8/18/77	5.10	12	11	19	13	39	6
<i>Sassafras albidium</i>	9/8/77	2.26	8	46 <sup>b</sup>	---	2	28	16
<i>Sonchus arvensis</i>	6/10/77	4.63	5	19	5	5	60 <sup>a</sup>	6
<i>Vernonia altissima</i>	5/23/77	2.62	13	12	2	4	68 <sup>a</sup>	1

<sup>a</sup>Prominent nonglyceride ester spot at RF ~0.6 in addition to the one at RF ~0.8.

<sup>b</sup>Prominent spot taken as free alcohol at RF ~0.23.

<sup>c</sup>Small spot at RF ~0.46 is unsaponifiable.

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