



Figure 1. Liquid chromatograms of II. (A) Calibration standard; 0.5 µg in 100-µL injection. (B) 10 × 100 µL injections of sample obtained from 50 g of cabbage spiked with 4 µg of I; extract diluted to 5.0 mL finally. (C) Same as (B) except that sample was onion. See the text for chromatograph conditions. The noise shown in this figure is schematic and has been exaggerated in two ways: the amplitude is too large by about a factor of 2 and the frequency is too low. We did not observe distinct noise spikes as drawn.

Table I. Recovery of Carbendazim (II) from Thiophanate Methyl (I)

sample	mass of I, µg ^c	recovery, % ^d
standard ^a	30 (2)	103 ± 4
	10 (1)	
	4 (2)	
onion ^b	100 (1)	91
	30 (4)	83 ± 5
	10 (3)	72 ± 3
	4 (2)	74 ± 3
cabbage ^b	100 (2)	82 ± 2
	30 (3)	72 ± 4
	10 (4)	70 ± 1
	4 (3)	77 ± 3

^a The conversion of I to II with no vegetable matter present. ^b Samples were 50 g of vegetable matter. ^c Mass of I added to sample and number of replicates in parentheses. ^d Average ± one standard deviation.

4 mL of 6.5 M NaOH and was extracted with four 50-mL portions of ethyl acetate saturated with water. The ethyl acetate solution was evaporated to 3–5 mL, 1 mL of 0.03 M H₃PO₄ was added, and the remaining ethyl acetate was removed. Finally, the volume was adjusted to 5.0 or 10.0 mL, depending on the mass of I added to the sample, by the addition of 0.03 M H₃PO₄. Samples of this solution

were analyzed for II with an LC fitted with a cation-exchange column and an absorbance detector as described above.

RESULTS AND DISCUSSION

Analyses were carried out for standard samples with no plant material present and for check samples in which various known amounts of I were added to 50-g samples of onion or cabbage. The results are listed in Table I. The standard samples gave conversions and recoveries of 103 ± 4%. The recoveries from onion and cabbage are incomplete, 68–91%, but are acceptable. There is a trend toward lower recoveries as the concentration of I in the vegetable matter decreases. At our lowest concentrations, 0.080 ppm, the signal-to-noise ratio was approximately 12 (see Figure 1) and the recovery was near 75%, comparable to recoveries reported by Shiga et al. (1977) for soils and by Ono et al. (1975) for vegetables. The limit of our method corresponds to samples with a concentration of 0.02 ppm for which the results suggest a signal-to-noise ratio of 3 and a recovery of about 65–70%. This detection limit is about the same as the limits reported by Shiga et al. (1977) for both I and II in soil, 0.03 ppm, by Ono et al. (1975) for vegetables, 0.02 ppm for I and 0.01 ppm for II, and by Gorbach (1980) for various plant materials, 0.02–0.06 ppm for II. The selectivity of our method is good, as can be seen in Figure 1.

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Natural Rubber from Sunflower. 2

The rubber content of the air-dried leaves of 31 wild species of sunflower (*Helianthus*) was determined by a gravimetric method. Ten species with a rubber content > 0.93% were further analyzed by ¹³C NMR spectroscopy. The extracts from the four species with the highest rubber content were >92% pure rubber. The benzene extract from the remaining species was contaminated by high molecular weight straight-chain hydrocarbons. Little or no rubber was found in the benzene extract from stems of these 10 species. Among the four species with the highest rubber content was *H. annuus*, the species from which commercial sunflower hybrid varieties are derived.

The profitable production of natural rubber from cultivated domestic plants is of considerable interest to agriculturalists to ensure an uninterrupted supply of this critical raw material. This is exemplified by the renewed

research effort in guayule production. General screening programs have discovered that members, other than guayule, of the Compositae family are capable of producing rubber. A prominent rubber-producing member of this

Table I. Rubber Content in Wild Sunflower Species

<i>Helianthus</i> species	collection site	plant part ^c	gravimetric, % rubber	¹³ C NMR	
				% rubber	% hydrocarbon
<i>radula</i>	Slidell, LA	L	1.93	1.89	0.04
<i>resinosus</i>	Collins, MS ^b	S	0.01		0.01
		L	1.93	1.78	0.15
<i>californicus</i>	Knoxville, CA ^b	S	0.08		0.08
		L	1.79	1.78	0.01
<i>debilis vestitus</i> ^a	Anna Maria, FL	S	0.10		0.10
		L	1.63	1.30	0.33
<i>debilis tardiflorus</i> ^a	Panacea, FL	S	0.01 ^d		
		L	1.55	1.10	0.45
<i>floridanus</i>	White City, FL	S	<0.01 ^d		
		L	1.53	1.19	0.34
<i>annuus</i>	Winton, OK	S	<0.01 ^d		
		L	1.45	1.40	0.05
<i>smithii</i>	Morganton, NC ^b	S	0.02		0.02
		L	1.40	0.58	0.82
<i>nuttallii nuttallii</i>	Louviers, CO ^b	S	0.03		0.03
		L	1.26	0.96	0.30
<i>arizonensis</i>	Snowflake, AZ ^b	S	0.12	0.04	0.08
		L	0.94	0.28	0.66
<i>heterophyllus</i>	Naveland, MS	S	0.31	0.04	0.27
		L	0.91		
<i>deserticola</i> ^a	Leeds, UT	L	0.82		
<i>debilis silvestris</i> ^a	Henderson, TX	L	0.77		
<i>giganteus</i>	Stem, NC	L	0.76		
<i>praecox praecox</i> ^a	La Porte, TX	L	0.71		
<i>debilis debilis</i> ^a	South Patrick Shores, FL	L	0.68		
<i>xlaetiflorus</i>	Sheridan, NE	L	0.66		
<i>eggertii</i>	Summertown, TN	L	0.64		
<i>ciliaris</i>	Bushland, TX	L	0.57		
<i>strumosus</i>	Silver City, NM ^b	L	0.55		
<i>pumilis</i>	Boulder, CO ^b	L	0.53	0.53	0.00
<i>praecox hirtus</i> ^a	Carrizo Springs, TX	L	0.49		
<i>occidentalis</i>	Raymondville, MO ^b	L	0.48		
<i>occidentalis</i>		L	0.42		
<i>silphioides</i>		S	0.04 ^d		
<i>laciniatus</i>	San Lorenzo, NM ^b	L	0.31		
<i>simulans</i>	Pensacola, FL ^b	L	0.31		
<i>hirsutus</i>	Poteau, OK ^b	L	0.30		
<i>praecox runyonii</i> ^a	Kingsville, TX	L	0.26		
<i>gracilentus</i>	Julian, CA	L	0.20		
<i>anomalous</i> ^a	Mexican Water, AZ	L	0.18		
<i>niveus canescens</i> ^a	El Paso, TX	L	0.16		

^a Annual species; all other species are perennial. ^b Analyzed material taken from a common nursery at Bushland, TX; all other material taken from their natural habitat. ^c L = leaves; S = stems. ^d Sample size precluded ¹³C NMR spectral analysis.

family is sunflowers (*Helianthus* spp.). In an earlier investigation (Stipanovic et al., 1980), we reported the occurrence of rubber in 23 sunflower species. We now report the natural rubber content of 30 additional wild species of sunflower.

MATERIALS AND METHODS

Plants collected at Bushland, TX, were grown under cultivation in a common nursery during the summer of 1980. Those collected at other sites were taken from their native habitats. Fresh green leaves and stems were air-dried, ground to a fine powder in a blender, and Soxhlet extracted successively with acetone and benzene by the procedure of Hall and Goodspeed (1919). The percentage of rubber in the plant was determined by weighing the residue from the benzene extraction. The gravimetric analysis of those species whose leaf rubber was >0.93% was repeated, and they were further analyzed by carbon-13 nuclear magnetic resonance spectroscopy (¹³C NMR); stems from these samples were also analyzed. The samples for ¹³C NMR were dissolved in CDCl₃ (the central peak, δ 76.9, of CDCl₃ was used as an internal standard). Peaks are reported in ppm (δ) downfield from tetramethylsilane.

The approximate concentration of hydrocarbons, which were present as a contaminant in the benzene extracts, was determined by comparing the ¹³C NMR spectra of an extract with and without a weighed amount of octacosane. Octacosane was used as a representative long-chain hydrocarbon.

RESULTS AND DISCUSSION

The amount of rubber in the 31 wild species of *Helianthus* are reported in Table I. The gravimetric analyses indicated that 10 species had rubber concentrations exceeding 0.93%. The values reported in Table I for these ten species are the average of two or more extractions. The benzene-soluble extracts for these 10 species were analyzed by ¹³C NMR. The ¹³C NMR analysis of extracts from stems of these species are also reported. The method used to calculate the rubber content in the benzene extracts is presented as supplementary material (see paragraph at end of paper regarding supplementary material).

The ¹³C NMR indicated that the benzene-soluble extracts were natural rubber contaminated with straight-chain hydrocarbons. The rubber gave peaks at δ 135.1, 125.0, 32.1, 26.3, and 23.3, and the hydrocarbons gave a

major peak at δ 29.6 in the ^{13}C NMR spectrum. A peak at δ 29.6 is characteristic of a high molecular weight straight-chain hydrocarbon. From these spectra, the percent rubber and percent hydrocarbon were calculated and are reported in Table I.

The benzene-extracted rubber fraction from six of these ten species was found to be contaminated with relatively large quantities of hydrocarbon. However, the four species (*H. radula*, *H. californicus*, *H. resinosus*, and *H. annuus*) giving the highest rubber content by the gravimetric method were relatively pure as analyzed by ^{13}C NMR spectroscopy. Our study further indicates that the rubber found in the aerial parts of the plant is concentrated in the leaves rather than in the stems. With two exceptions (*H. arizonensis* and *H. nuttallii nuttallii*), the benzene extract from stems was composed entirely of the straight-chain hydrocarbons.

We earlier reported that cultivated hybrid varieties "894" and "896" had a foliar rubber content of 0.49% and 0.74%, respectively (Stipanovic et al., 1980). Since all cultivated sunflower hybrids are derived from *H. annuus*, it is especially noteworthy that the *H. annuus* collected from Winton, OK, had a rubber content of 1.45%. Bruehrer and Benson (1945) reported a rubber content of 0.55% from *H. annuus* collected at Tucson, AZ, while Minshall (1957) reported that *H. annuus* plants collected at Ontario, Canada, contained 0.26% rubber. The reasons for these differences are uncertain and will require additional study. Our results indicate that there is a high potential for increasing the rubber content of cultivated sunflower. In view of the current interest in a domestic source of natural rubber, the potential of sunflower deserves additional study.

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Supplementary Material Available: Method and equation used to calculate the percent hydrocarbon present in the benzene extracts (1 page). Ordering information is given on any current masthead page.

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Chemical Ionization Mass Spectra of Aldicarb and Metabolites

The isobutane chemical ionization mass spectra of aldicarb [2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbonyl)oxime] and of its metabolites aldicarb sulfoxide and aldicarb sulfone show strong $(\text{M} + \text{H})^+$ signals and also large peaks due to the corresponding ions of the protonated oxime and nitrile moieties. These results are of distinct diagnostic and analytical value.

Aldicarb is a widely used systemic pesticide with combined insecticidal, nematicidal, and miticidal properties (U.S. Environmental Protection Agency, 1975). Trace analysis of environmental samples of aldicarb and its toxic metabolites (sulfoxide and sulfone) represents an important but complicated problem. This is due to the considerable reactivity and thermal instability of these molecules, which in the case of gas chromatography (GC) results in decomposition (Hall and Harris, 1979) of the measured molecules. In the case of mass spectrometry (MS) the lability of these compounds prevents the observation of their molecular ions in electron impact mass spectrometric (EI-MS) assays. Thus in the EI-MS studies of aldicarb and of its two oxidation products (Benson and Damico, 1968), no molecular ions M^+ were reported. The major fragmentation pathway in the EI-MS is the C-S bond cleavage rather than that giving rise to the methyl isocyanate fragment.

Although not observable by electron ionization, the molecular ion of aldicarb sulfone (only) could be observed by field ionization (Damico et al., 1969) and that of aldicarb

itself was seen by field desorption measurements (Fales et al., 1975). Earlier CI studies of aldicarb (Fales et al., 1975; Holmstead and Casida, 1975) gave no evidence for the protonated molecular $(\text{M} + \text{H})^+$ ion. In the present communication we report the results of an isobutane CI-MS study of aldicarb and its metabolites. This ionization method provides abundant $(\text{M} + \text{H})^+$ ions as well as several diagnostic ions which may prove useful for residue and metabolism studies.

EXPERIMENTAL SECTION

Reagents. Analytically pure samples of aldicarb, aldicarb sulfoxide, and aldicarb sulfone, supplied by the Union Carbide Corp., were provided by Dr. I. Adato (Ministry of Agriculture, Jaffa) and continuously stored at -20°C .

Mass Spectrometry. Mass spectra were recorded on our low-resolution single-focusing Du Pont 21-490B instrument and repeated on the Du Pont 21-490B instrument of Dr. S. Zitrin (Israeli Police Laboratory, Jerusalem). These instruments are equipped with a dual EI/CI ion