Natural Rubber from Sunflower

Carbon-13 nuclear magnetic resonance was used to detect natural rubber in extracts from wild and domestic sunflowers. The rubber content of 23 wild species, 2 commercial varieties, and 1 wild hybrid was determined by benzene extraction and is tabulated. Two wild species, *Helianthus agrestis* and *H. occidentalis*, contain 1.6% rubber in their foliar parts. It is estimated that 20 lb of rubber per acre could be obtained from one of the commercial varieties tested. The feasibility of using sunflower as a commercial source of rubber is discussed.

The current concern about the availability of petroleum resources from foreign markets has stimulated studies that focus on obtaining these products from alternate sources. In agriculture, the emphasis has been on the use of agricultural residues as potential sources of energy and on the development of exotic or little-utilized plant species as substitutes for petrochemicals. Examples are the burning of cotton gin trash to provide energy for ginning and drying cotton seed cotton (Oursbourn et al., 1978) and fermentation of sugarcane, corn, or small grains to produce alcohols. Natural rubber from guayule is prominent among plant products intended for partial replacement of petrochemicals (Lopez et al., 1978).

Current research on plant-derived substitutes for petrochemicals is largely focused on the cultivation of species that are not presently used as agricultural crops. The introduction of new crops presents an array of problems that are costly and time consuming to solve.

During our investigation of wild and domestic sunflower plants (*Helianthus* spp.), we isolated considerable amounts of a polymeric compound. Analysis of this compound by carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy showed that it was natural rubber. In view of the current interest in phytochemical substitutes for petrochemicals, we analyzed a number of wild and domestic sunflower species for their rubber content. Although several references to the presence of rubber in sunflowers are scattered throughout the literature, this is the first extensive study of this genus.

MATERIALS AND METHODS

Plants collected at Bushland, TX, were grown under cultivation in rows. Those collected at other sites were taken from their native habitats. Green, air-dried leaves or stems were ground to a fine powder in a blender and soxhlet extracted successively with acetone and benzene by using the procedure of Hall and Goodspeed (1919). The weight of the residue from the benzene-soluble fraction was used to determine the percentage of rubber in the plant.

RESULTS AND DISCUSSION

The ^{13}C NMR spectrum (C_6D_6 was used as solvent and the central peak, δ 128.0, was used as an internal reference) of the benzene-soluble fraction gave peaks at δ 135.1 (s), 124.9 (d), 32.1 (t), 26.3 (t), and 23.3 (q), observations which agreed with those of Duch and Grant (1970) for rubber. The ^{13}C NMR data confirmed that natural rubber was the major component in the benzene-soluble residue, and the residue was contaminated with only trace quantities of other components. ^{13}C NMR analyses were performed on three species chosen at random.

Earlier surveys of plant families reported the occurrence of rubber in five species of sunflower (Vorob'eva, 1940; Mitchell et al., 1942; Bruehrer and Benson, 1945; Minshall, 1957), but these reports apparently did not prompt an optimistic view of sunflower as a practical commercial source of rubber. After examining 206 plant species (two of which were sunflower species) growing in the central United States, Swanson et al. (1979) reported that the rubber in *H. hirsutus* had an average molecular weight and polydispersity factor that could produce a potentially useful natural rubber.

Table I. Rubber Content of Sunflower Species (*Helianthus*, spp.)

plant	location	plant part[a]	% rubber
H. agrestis	Bushland, TX	L	1.66
H. occidentalis-plantagineus	Bushland, TX	L	1.62
H. argophyllus[b]	Gonzales, TX	L	1.14
H. tuberosus	Bushland, TX	L	0.93
Hybrid-896	Bushland, TX	L	0.74
H. atrorubens[c]	Clemson, SC	L	0.68
H. annuus[d]	Tucson, AZ	L	0.55
H. debilis-cucumerifolius	Halletsville, TX	L	0.52
H. niveus-canescens	Bushland, TX	L	0.50
Hybrid-894	Bushland, TX	L	0.49
H. divaricatus[e]	Carleton Co., ON	W	0.47
H. argophyllus x H. annuus	Bushland, TX	L	0.40
H. salicifolius	Bushland, TX	L	0.37
H. mollis	Bushland, TX	L	0.31
H. exilis[b]	Bushland, TX	L	0.31
H. petiolaris-fallax	Bushland, TX	L	0.30
H. grosseserratus	Bushland, TX	L	0.28
H. microcephallus[b]	Bushland, TX	L	0.26
H. argophyllus	Bushland, TX	L	0.26
H. annuus[e]	Ottawa, ON	Sh	0.26
H. glaucophyllus	Bushland, TX	L	0.25
H. maximiliani	Bushland, TX	L	0.24
H. angustifolius	Bushland, TX	L	0.18
H. paradoxus	Bushland, TX	L	0.15
H. petiolaris-petiolaris	Clarendon, TX	L	0.14
H. longifolius	Bushland, TX	L	0.13
H. neglectus	Bushland, TX	L	0.10
Hybrid-894	Bushland, TX	S	0.09
H. tuberosus[e]	Ottawa, ON	Sh	0.08

[a] L = green leaves; S = stems; Sh = shoots; W = whole. [b] Benzene extract analyzed by ^{13}C NMR spectroscopy. [c] Mitchell et al. (1942). [d] Bruehrer and Benson (1945). [e] Minshall (1957).

The results of our survey are summarized in Table I. Of the species surveyed, *H. occidentalis* and *H. agrestis* gave the highest yield (1.6%) of rubber while several other species gave only trace quantities. In order to estimate potential yields, two commercial varieties of sunflowers, Hybrid-896 and Hybrid-894, were chosen at random for analysis. Although the two varieties are generally considered to be genetically similar, their rubber content was quite different. Assuming 20 000 plants/acre, we estimate that Hybrid-896 would yield 20 lb of rubber per acre; this yield is considerably below the optimistic yield (600 lb/acre) projected for guayule. However, several other factors

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must be weighed when considering rubber production from sunflower.

No attempt has been made to maximize the potential of rubber content through breeding nor to evaluate the remaining 31 species of *Helianthus*. The rubber content of the two closely related commercial varieties, Hybrid-896 and Hybrid-894, indicated that a wide variation occurs when no attempt is made to maximize rubber yields; thus, the potential for improvement exists. Our analysis also showed that the ornamental Mexican sunflower (*Tithonia rotundifolia*) has over 2% of a lower molecular weight rubber. Moreover, sunflower is already a profitable crop. Breeding techniques, planting methods, environmental influences, and major pests are already known.

Rubber production from sunflower could be an economic bonus. The residue from the plant extraction might also be a useful commodity, since residues of sunflower plants are ranked near the top for btu value (Oursbourn et al., 1978). Thus, a facility for processing rubber from sunflower might also be an ideal site for energy production from biomass. Additional research is needed to completely assess the potential of rubber production from sunflower.

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Direct Analysis of the Wild Oat Herbicide, Asulam, in Wheat Samples by Reversed-Phase Liquid Chromatography at Selected Ultraviolet Wavelengths

The wild oat herbicide asulam (methyl *N*-(4-aminobenzenesulfonyl)carbamate) was extracted from whole and refined wheat flour and whole wheat cereal with acetonitrile. An aliquot of the extract was partitioned with hexane which removed much of the lipophilic coextractives. The acetonitrile layer was then evaporated to about 0.2 mL and diluted with mobile phase to 1.0 mL for liquid chromatographic analysis. Separation of asulam from other sample components was achieved with a Lichrosorb RP-8 column and a mobile phase consisting of 20% (v/v) acetonitrile in water containing 0.1% acetic acid. Detection limits were estimated to be 0.02–0.05 ppm with an average recovery of about 87% over the range 0.1–10.0 ppm in the products studied.

INTRODUCTION

Asulam (methyl *N*-(4-aminobenzenesulfonyl)carbamate) is a systemic herbicide used in the prairie regions of Canada for the control of wild oats in cereal grains such as wheat. It is one of the five wild oat herbicides which accounted for about 50% by weight of all pesticides used in Canada in 1976. At the moment, the only methods available for asulam determination are a colorimetric procedure which employs diazotization with *N*-(1-naphthyl)ethylenediamine (Brockelsby and Muggleton, 1973) and a gas chromatographic (GC) technique (Bardalaye et al., 1979) which involves hydrolysis and derivatization. We describe in this paper a liquid chromatographic (LC) method which is capable of determining asulam in wheat products without derivatization. As a result the technique is simpler and more rapid than either of the above-mentioned techniques and may be easily incorporated into routine pesticide screening programs. The approach is intended to serve as a part of a direct LC multiresidue screening technique for all five wild oat herbicides in cereal grain products.

EXPERIMENTAL PROCEDURES

Reagents. Distilled-in-glass grade solvents were used for sample extraction and preparation of the standards. Stock solutions of asulam were prepared in acetonitrile at a concentration of 1.0 mg/mL. Spiking solutions were prepared from this by diluting with acetonitrile as required. Standards for LC were prepared by dilution of the stock with the mobile phase.

The wheat products examined were whole wheat cereal and whole and refined wheat flour.

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