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Guayule Byproduct Evaluation: Extract Characterization

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Composition profiles have been made of the water and acetone extracts of guayule woody tissue. Extractables from cultivars 593, N575, N576, 11634, 11635, and 12229 were surveyed. The major acetone extract components assayed were sesquiterpene esters (10–15%), triterpenoids (27%), and fatty acid triglycerides (7–19%). Sesquiterpene ester levels reflected processing heat history. All major extract triterpenoids were found to be C_{30} compounds. Dilute acid hydrolysis of aqueous extract polysaccharides (63% of the extract) did not provide a good source of fermentable sugars.

As a renewable, native source of natural rubber (Campos-Lopez et al., 1979; Eagle, 1981), guayule [*Parthenium argentatum* (Gray)] is undergoing careful economic assessment. Current processing employs acetone to extract resinous components from the milled shrub or coagulated latex (Eagle, 1981). For every kilogram of rubber there can be one or more kilograms of resin (Buchanan et al., 1978; Burlett et al., 1981). Marketing high-value resin-based byproducts could significantly reduce guayule rubber manufacturing costs. Characterizing resin composition is necessary to determine optimum utilization. Consequently, byproduct evaluation should be consistent with commercially feasible processing.

A variety of secondary metabolites can be extracted from guayule. These include non-rubber isoprenoids such as terpenes and sesquiterpenes (Haagen-Smit and Siu, 1944), sesquiterpene esters (guayulins A and B) (Romo et al., 1970; Proksch et al., 1981), diterpene ketoalcohols (Dorado Bernal et al., 1962), phytosterols (Buchanan et al., 1978; Klein and Pirschle, 1923; Schmid and Stoehr, 1926), and triterpene ketoalcohols (argentatins A, B, and C) (Rodriguez-Hahn et al., 1970). Fatty acid triglycerides have been saponified and the acids characterized (Buchanan et al., 1978; Keller et al., 1981; Belmares et al., 1980). Polyphenolics (Buchanan et al., 1978), including leaf flavonoids and flavonoid glycosides (Mears, 1980), have been identified. In addition, there exists a wide range of water extractables including proteins (Banigan et al., 1982) and mono- and polysaccharides (Banigan et al., 1982; Traub and Slattery, 1946).

We report here the quantitation of some major components and component classes in the acetone and water extracts of guayule woody tissue. Non-rubber isoprenoid component compositions are detailed. While our primary emphasis was on characterizing cultivar 593 extractables, survey analyses were also run for cross comparison of extracts from several other cultivars.

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Table I. Shrub Procurement and Woody Tissue Extraction

cultivar	source[a]	time of harvest	age at harvest, year[b]	extract yield, wt % aqueous	extract yield, wt % organic
593	UA	3/81	3	15.0	6.5
593	LA	4/81	4	14.5	7.4
593	LA	9/81	4		
N575	UA	8/81	3.25		
N576	UA	8/81	4		
11634	LA	9/81	4	9.5	11.0
11635	LA	9/81	4		
12229	UA	8/81	4		

[a] UA: University of Arizona, Tucson, AZ; LA: Los Angeles State and County Arboretum, Arcadia, CA. [b] Includes 1 year in greenhouse prior to field transplant.

EXPERIMENTAL SECTION

Shrub Procurement. Guayule shrub samples were provided from cultivated plots in Arizona and California. Table I summarizes procurement data.

Shrub Processing and Extraction. Shrub was manually defoliated, mechanically chipped, and then passed through an 8-in. single disk attrition mill. Resin samples were obtained by exhaustive extraction of milled woody tissue. Typically, a 450-g sample of milled guayule was extracted with four 1-L aliquots of water previously heated to boiling. The combined extracts, usually 2–3% solids, were desolventized at 40 °C under vacuum to give a tan, resinous residue. Anal. Found: C, 41.59; H, 5.97; N, 3.85; P, 1.45; Ca, 2.79; Na, 1.36; Mg, 0.62. Acetone extractions

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Table II. Organic Extract Non-Rubber Isoprenoids and Triglycerides from Various Cultivars

component	wt %					
	593	N575	N576	11634	11635	12229
terpenes, sesquiterpenes	1	1	1	2	2	1
guayulin A	9	10	10	9	10	8
guayulin B	2	2	1	2	3	1
sesquiterpene cinnamate C	3	1	1	1	1	1
sesquiterpene anisate D	1	*a*	*a*	*a*	*a*	*a*
argentatin A	8	17	12	15	14	12
argentatin B	4	7	4	6	6	5
argentatin C	1	*b*	*b*	*b*	*b*	*b*
triterpenoid D	3	5	4	4	5	4
sterol glycosides	2	*b*	*b*	*b*	*b*	*b*
other phytosterols,[c] triterpenoids	9	*b*	*b*	*b*	*b*	*b*
fatty acid triglycerides	13	7	18	19	7	13

[a] Less than 0.5%. [b] Not determined for this cultivar. [c] Includes β-sitosterol.

used three 1-L aliquots percolated through 570 g of air-dried, water-extracted bush, the last aliquot through being used to extract any subsequent bush sample. Solvent removal left a green, viscous oil. Anal. Found: C, 76.56; H, 10.09; N, 0.30; Ca, 0.13. Table I gives typical extract yields. Additional resin for partition method development was obtained from the CIQA pilot plant, Saltillo, Mexico.

Extract Characterization. Elemental analyses (C, H, N, P) were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI. Metal content determinations were made by atomic absorption spectroscopy of ashed samples. A Finnigan Model 4000 mass spectrometer/data system was used for direct probe and capillary GC/MS of volatile hydrocarbons. Direct probe mass determinations were also made on a CEC 21-110C mass spectrometer with perfluorokerosene as the internal standard. ^{1}H (60 MHz) and ^{13}C (20 MHz) NMR spectra were obtained for samples in $CDCl_3$ solution with tetramethylsilane as an internal standard.

Extract Component Quantitation. Organic extract triglycerides were determined by high-efficiency gel permeation chromatography (GPC) in tetrahydrofuran (THF) using a series of two Varian 30-cm MicroPak TSK G3000H8 and two 30-cm TSK G2000H8 columns, with trilinolein as the external standard. Differential refractive index and UV (254 nm) detectors were used for quantitation. Organic extract HPLC analyses used a Varian MicroPak MCH-10 column. Guayulins were quantified by using an acetonitrile–water gradient going from 50:50 to 75:25 over 5 min and then held at 75:25; UV detection was at 262 nm. Ethyl *p*-anisate was run as the internal standard. Argentatins A and B and triterpenoid D were initially quantified as the 2,4-dinitrophenylhydrazones (DNPH) by using *tert*-butylcyclohexanone DNPH as the external standard. These HPLC analyses were run by using 60:40 THF–water with UV detection at 371 nm. The DNPH derivatives of argentatin B and triterpenoid D were not resolved under these conditions; consequently, the relative levels of the two underivatized triterpenoids were determined by using 58:42 acetonitrile–water with UV detection at 220 nm. Sesquiterpene alcohols and other triterpenoids were determined by gas chromatography (GC) on a 3 ft. × 0.08 in. i.d. column of 3% SP-2250 on 100–120-mesh Supelcoport programmed from 100 to 280 °C at 10 °C/min. β-Sitosterol was used as the external standard. Sterol glycosides were estimated from composition changes in the organic extract after dilute acid hydrolysis. Terpenes and sesquiterpenes were determined by GC using a 6 ft × 0.125 in. o.d. column of 5% SE-30 on Chromosorb W programmed from 100 to 280 °C at 10 °C/min. Fatty acids, with behenic acid as the internal standard, were treated with diazomethane; the resulting methyl esters were analyzed by GC using a 6 ft × 0.125 in. o.d. column of 5% DEGS on 100–120-mesh Chromosorb G-HP at 200 °C. Aromatic acids were determined by NMR: the anisate methyl and cinnamate olefinic proton signals were compared to that of the nitromethane internal standard. The aqueous extract and polysaccharide hydrolysate, with xylitol as the internal standard, were analyzed by HPLC at 85 °C using a Bio-Rad HPX-87 carbohydrate column.

Table III. Organic Acid Compositions

acid	component wt %			
	593[a]	593[a]	CIQA[b]	CIQA[c]
cinnamic	25	16	28	9
p-anisic	3	7	*d*	*d*
palmitic	15	10	5	9
stearic	2	1	4	1
oleic	5	4	4	9
linoleic	36	44	47	58
linolenic	12	18	12	13

[a] Cultivar 593, this work. [b] CIQA (Saltillo) resin (Keller et al., 1981). [c] CIQA (Saltillo) resin (Belmares et al., 1980). [d] Not reported.

Table II provides a comparison of organic extract compositions from several cultivars. In addition to the components listed, the organic extracts contain low-volatility material with molecular weights of 500–800, as inferred from GC and GPC analyses.

Organic Extract Saponification. Crude cultivar 593 organic extract was dissolved in two parts (w/w) of toluene or THF and filtered through Celite to remove insolubles. Filtrate desolventization gave material for whole-resin analysis. The extract saponification procedure was essentially that of Keller et al. (1981), modified according to Meeks and Banigan (1956). Recovered neutrals, 52 g/100 g of extract, contained 14% sesquiterpene alcohols and 55% phytosterols and triterpenoids. The crude organic acid fraction, 28 g/100 g of extract, contained 57% carboxylic acids. Table III details acid compositions.

Guayulins. Crude bicyclogermacren-9-ol (BG-9-OL), bp 125–135 °C (10 Pa), was obtained from the saponification neutral fraction by short path distillation. Hexane recrystallization gave fine, colorless needles, mp 127–129 °C [lit. (Romo et al., 1970) mp 129–130 °C]. Overnight room temperature esterifications used 1.5 g (6.8 mmol) of BG-9-OL and 7.5 mmol of cinnamoyl chloride (for guayulin A) or *p*-anisoyl chloride (guayulin B) in 3.3 g (41.7 mmol) of dry pyridine. Workup followed by chromatography on alumina and cyclohexane recrystallization gave material suitable for NMR analysis. Guayulin A: colorless prisms, mp 121–123 °C [lit. (Romo et al., 1970) mp 122–123 °C]; mass spectrum m/z 350.2240, calcd for $C_{24}H_{30}O_2$ 350.2246.

Guayulin B: colorless needles, mp 123.5–125 °C [lit. (Romo et al., 1970) mp 125–126 °C); mass spectrum m/z 354.2191, calcd for $C_{23}H_{30}O_3$ 354.2195. The ^1H NMR (Romo et al., 1970; Rodriguez et al., 1981) and IR (Romo et al., 1970) spectra, as well as GC and HPLC retentions, of the synthesized esters correspond to those of the guayulins in unsaponified resin.

Sesquiterpene Cinnamate C. Four samples of organic extract, a 22.6-g total, were loaded on a 25 × 250 mm column of 70–230-mesh silica gel (Merck type 60). The samples were chromatographed following the sequence carbon tetrachloride, 200 mL, benzene, 240 mL, chloroform, 600 mL, and THF, 240 mL. Chloroform effluent fractions 12–26 (40 mL each) gave 7.60 g of material. This was rechromatographed following the sequence benzene–chloroform (70:30), 1600 mL; chloroform, 1000 mL; and THF, 400 mL. Effluent fractions 18–30 (40 mL each) gave 1.88 g of material, which was loaded on a 10 × 450 mm water-jacketed silica gel column and chromatographed at 20 °C with 400 mL of benzene–chloroform (75:25). In this final step, effluent fractions 10–17 (20 mL each) gave 1.06 g of residual material containing the cinnamate ester as a major component. Fraction 14, affording 159 mg of residue, had the highest cinnamate ester concentration. Sesquiterpene cinnamate C had mass spectrum m/z 366.2153, calcd for $C_{24}H_{30}O_3$ 366.2195. Reaction with trifluoroacetic anhydride produced a trifluoroacetate: mass spectrum m/z 462.1979, calcd for $C_{26}H_{29}F_3O_4$ 462.2018. The sample contained 20–25 mol % argentatin B.

Argentatins. Authentic samples of argentatins A, B, and C were provided by A. Romo de Vivar, National University of Mexico (UNAM). Argentatin A mass spectrum m/z 472.3534, calcd for $C_{30}H_{48}O_4$ 472.3552; m/z (rel intensity) 472 (1, M^+) and 143 (100, M − 329). Argentatin B mass spectrum m/z 456.3594, calcd for $C_{30}H_{48}O_3$ 456.3603; m/z (rel intensity) 456 (1, M^+), 397 (50, M − 59), and 59 (100). Argentatin C mass spectrum m/z 454.3344, calcd for $C_{30}H_{46}O_3$ 454.3447; m/z (rel intensity) 455 (6), 454 (19), 439 (22), and 43 (100).

Triterpenoid D. A 10-g sample of saponification neutral fraction, from which BG-9-OL had been distilled, was loaded on a 10 × 200 mm column of 80–325-mesh alumina (13.73% moisture content). The samples were chromatographed with 95:5 benzene–ethyl acetate. The first two 40-mL fractions gave 2.0 g of crude triterpenoids. Hexane recrystallization yielded 1.2 g of mixed argentatin B and triterpenoid D. Argentatin B was isolated from this material as a first crop from cyclohexane. Methanol recrystallization of the material remaining in the cyclohexane mother liquor gave triterpenoid D as colorless needles, mp 160–161.5 °C; mass spectrum m/z 456.3608, calcd for $C_{30}H_{48}O_3$ 456.3603; m/z (rel intensity) 456 (15, M^+), 397 (100, M − 59), and 59 (9).

Aqueous Extract Partition and Hydrolysis. Crude undesolventized cultivar 593 aqueous extract, equivalent to 45.7 g of solids, was treated with 190 mL of 0.5 F $Pb(OAc)_2$ to remove polyphenolics. Excess lead salts were removed with H_2S. Desolventizing the polyphenolic-free extract solution gave 29.0 g (63%) of crude polysaccharides as a reddish orange resin. The polysaccharides were hydrolyzed according to Traub and Slattery (1946). Hydrolysate hexose was fermented over 17.5 h with brewer's yeast to give 1.8 mmol of ethanol/g of hydrolysate.

RESULTS AND DISCUSSION

Extract yields (Table I) were determined for a few shrub samples. Cultivar 593 aqueous extract yields of 17–23% and organic extract yields of 6–8% have been reported by Burlett et al. (1981). Unextracted woody tissue typically contained 0.77% calcium. This is consistent with earlier estimates (Swett, 1909). As expected, the aqueous extract contained the greater proportion of metal salts.

Table IV. Effect of Processing Temperatures on Organic Extract Sesquiterpene Esters

component	component wt %		
	unmilled[a]	T_{max} = 100 °C[b]	T_{max} = 200 °C[b]
sesquiterpene anisate D	c	0.9	0.8
sesquiterpene cinnamate C	c	2.8	2.0
guayulin B	2.1	2.2	1.6
guayulin A	10.2	9.2	5.5

[a] From HPLC data in Proksch et al. (1981). [b] Desolventization temperature upper limit (see Experimental Section), milled woody tissue extract. [c] Not reported.

In the organic extracts, the major components quantified (Table II) were sesquiterpene esters, triterpenoids, and triglycerides. These extract compositions are in part processing artifacts. Hydrocarbon volatilization has been recognized as a source of compositional variation (Buchanan et al., 1978). In our processing scheme, woody tissue milling could produce enough localized heating to volatilize some terpene components. The sesquiterpene esters also reflect processing heat history. Esters C, a C_{15} cinnamate, and D, a C_{15} p-anisate, were found in all the organic extracts we analyzed. The relative yield of these esters, compared to that of the guayulins, was highest when extract workup temperatures exceeded 150 °C (Table IV). Heating the desolventized extract at 150 °C in air also increased the proportion of esters C and D. Secondary product formation reduced the total sesquiterpene ester content. Sufficient ester C was isolated to establish its composition. ^{13}C NMR indicates an isopropenyl substituent (C-1 at 110.0, C-2 at 147.4, and C-3 at 20.7 ppm) and two carbons singly bonded to oxygen (72.5 and 80.0 ppm). This component forms a trifluoroacetate, indicating a free hydroxyl group. Neither Rodriguez et al. (1981) nor we have detected any sesquiterpene derivatives corresponding in structure to "partheniols" or "parthenyl cinnamates" (Walter, 1944; Haagen-Smit and Fong, 1948; Hendrickson and Rees, 1962).

The argentatins are major triterpenoid components. We found all three argentatins to be C_{30} compounds. Argentatins B and C have been previously described (Rodriguez-Hahn et al., 1970) as C_{31} compounds. Argentatin A has a mass spectrum base peak at m/z 143 (M − 329), consistent with its assigned structure. Argentatin B has a mass spectrum base peak at m/z 59 (M − 397), suggesting a demethyl analogue of the assigned structure. We suspect the composition we obtained for argentatin C may be that of a dehydration product. Triterpenoid D, a previously unreported extract component, exhibits HPLC behavior and a mass spectrum consistent with its being a closely related isomer of argentatin B.

Cultivar 593 organic acid compositions varied (Table III), indirectly reflecting sesquiterpene ester and triglyceride levels and distributions. In all cases, the major aromatic acid was cinnamic acid and the major fatty acid was linoleic acid.

We have seen that organic extract yields vary with cultivation site, harvest date, and shrub strain. Table II compares component distributions for several cultivars. Variations were especially pronounced in sesquiterpene ester distributions and fatty acid triglyceride levels. Since all samples were worked up similarly, these variations are significant. An across the board multistrain comparison

is not possible because of agronomic factor variations (Table I). Sample consolidation needed for scaled up resin extractions precluded comparing the various cultivar 593 shipments. However, cultivar pair N576 and 12229 and cultivar pair 11634 and 11635 have cultivation and harvest histories similar enough for comparison of component distributions.

Buchanan et al. (1978) reported 7.1% polyphenolics (tannins and flavonoids) in whole plant extract. We found that polyphenolics, 37% of the aqueous extract, correspond to 5% of cultivar 593 woody tissue. The crude polysaccharide fraction, 9–10% of cultivar 593 woody tissue, is a mixture reported to contain extractable levulins, inulins, and monosaccharides (Traub and Slattery, 1946), among other non-phenolic polar components. Dilute acid hydrolysis of this fraction gave a multicomponent mixture. The most abundant monosaccharide, slowly fermented by brewer's yeast, had an HPLC retention corresponding to that of mannose. A relatively low level of arabinose was also observed. No fructose was detected. The polysaccharide fraction is not a good source of fermentable sugars.

Our program's sampling and processing protocols were directed toward woody tissue extract analysis; whole shrub extracts would require further characterization. Extract yield and composition will depend on shrub strain, cultivation history, and processing procedures. In addition, seasonal shifts in secondary metabolite distributions have been noted for guayule (Meeks et al., 1950; Lloyd, 1911). A more comprehensive extract composition profile must take this seasonal variation into account.

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Registry No. Guayuline A, 31685-97-9; guayuline B, 31685-98-0; argentatin A, 31324-30-8; argentatin B, 31300-41-1; argentatin C, 31300-42-2.

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Influence of pH and Light on the Kinetics of Vitamin B_6 Degradation

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A method based on ioning pairing high-performance liquid chromatorgraphy was used to measure the stability of pyridoxine (PN), pyridoxal (PL), and pyridoxamine (PM). Kinetic analysis was used to compare the influence of various factors on the rate constants. In buffered solution in the pH range of 4–7, PN showed very little degradation while PM and PL showed a strong influence of pH on loss rates. In a dry model system exposed to different temperatures, water activities, and light, loss of PL was significantly influenced by storage temperature and light.

The instability of vitamin B_6 during processing and storage can contribute to losses of the nutritional quality of foods. This vitamin can occur as pyridoxine (PN), pyridoxal (PL), pyridoxamine (PM, and the phosphorylated forms of these compounds. Since the various forms do not have the same stability (Hassinen et al., 1954; Gregory and Kirk, 1978a; Ang, 1979), an evaluation of the loss reactions must take into account the reactivity of each vitamer.

While B_6 is recognized as an unstable vitamin (Harris and Karmas, 1975), few studies have taken a kinetic approach to evaluate the factors that influence the stability of vitamin B_6. Gregory and Kirk (1978a) demonstrated that the degradation of various B_6 vitamers in a model

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