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Tannin signatures of barks, needles, leaves, cones, and wood at the molecular level

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Abstract—We analyzed 117 tissues from 77 different plant species for molecular tannin. Tannin was measured in 89 tissues (as high as 10.5 wt.% total tannin), including procyanidin (PC) tannin in 88 tissues, prodelphinidin (PD) tannin in 50, and propelargonidin (PP) tannin in 24. In addition to tannin, several flavones, flavanones, and triterpenoids were measured, the latter which yielded as much as 4.5 wt.%. Compositions varied considerably between species, including several that yielded comparatively rare tannin or triterpenoids. Conifer needles were distinguished by high yields of PD tannin overall and relative to PC tannin. Dicotyledon leaves were characterized by the presence of flavones and triterpenoids. Barks were marked by flavanones and tetracosanoic acid. Based on these trends, relationships that could be useful as geochemical parameters were developed for distinguishing needles, leaves, and barks as possible components of litter, soil, or sedimentary mixtures. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

The environmental reactivity of tannin, combined with its abundance and ubiquity in vascular plants (Haslam, 1989), makes it a prime candidate for biogeochemical studies. In terrestrial biomass, tannin trails only carbohydrates (in the form of cellulose and hemicellulose) and lignin in overall abundance, as the latter are the primary components in woody tissues. However, in soft tissues such as leaves, needles, and bark, tannin is often more abundant than lignin (Hedges and Weliky, 1989; Kelsey and Harmon, 1989; Benner et al., 1990). Because these tissues cycle more rapidly than woods, tannin can be quantitatively, as well as qualitatively, important in early diagenesis (Benner et al., 1990; Hernes et al., 2001).

Tannin is found only in vascular plant tissues and occurs in both condensed and hydrolyzable forms (Fig. 1). Condensed tannins are polymers and oligomers of three-ring flavanols, of which there are at least a dozen known variants. The components are typically labeled “extender” or “terminal” units depending on their location (Fig. 1). Linkages of tannin monomers are most commonly 4→8, but 4→6 linkages also regularly occur which leads to branching (Fig. 1). Polymers and oligomers with these linkages form a subset of condensed tannin known as proanthocyanidins (PA) because of their proclivity toward the formation of cyanidins and related compounds when acid depolymerized. Rarer linkages include A to A-ring and A to B-ring linkages which are not PA. More complete reviews of the chemistry and structure of condensed tannin can be found elsewhere (Hemingway, 1988a,b; McGraw, 1988; Laks, 1988). Hydrolyzable tannin is made up of gallic acid units or its derivatives, often ester-linked to polyols such as glucose (Fig. 1). With its structural diversity and phenolic character, tannin participates in a number of important reactions, including photochemical and redox transformations, nitrogen immobilization, and cation complexation. Tannins are also potential precursors of humic substances via quinone formation and Schiff base reactions.

While the natural products literature contains numerous molecular-level characterizations of tannin from different source materials (e.g., Thompson et al., 1972; Harborne, 1988; Mole, 1993), the results of these analyses are difficult to use as source indicators in biogeochemical studies due to lack of a standardized analytical procedure, representation among the biogeochemically important tissue types, and definitive quantification. Nevertheless, several molecular trends are evident in the tannin literature that might be useful and complementary to applications of lignin and cutin (also uniquely terrestrial) as biomarkers. For instance, lignin is not used to distinguish monocotyledons and dicotyledons, whereas *ent*-epicatechin is unique to monocotyledons, and propelargonidin-containing polymers are much more common in monocotyledons than dicotyledons (Ellis et al., 1983). In addition, hydrolyzable tannin is only found in dicotyledons. Although the geochemistry of bark is poorly studied, some barks have been shown to contain large quantities of flavanones (Hergert, 1989). Barks are also important industrially and anthropogenically, as debarking waste generated by the timber industry often contains toxic levels of tannin (Field and Lettinga, 1992). Finally, in certain environments where potential sources are more constrained, condensed tannin compositions often provide more species-dependent taxonomic information (Haslam, 1989).

This study utilizes a recently developed molecular tannin method (Hernes and Hedges, 2000) that combines reproducible quantification along with rapid throughput to evaluate the source potential of various plant tissues in biogeochemical studies. We analyzed 117 different source materials from tropical and temperate monocotyledons, dicotyledons, and conifers, including 18 barks, 16 woods, 7 cones and seedpods, and over 70 leaves, needles, and whole plants. In addition to molecular tannin compounds, several triterpenoids and carboxylic acids also fall within the analytical window and provide additional source information.

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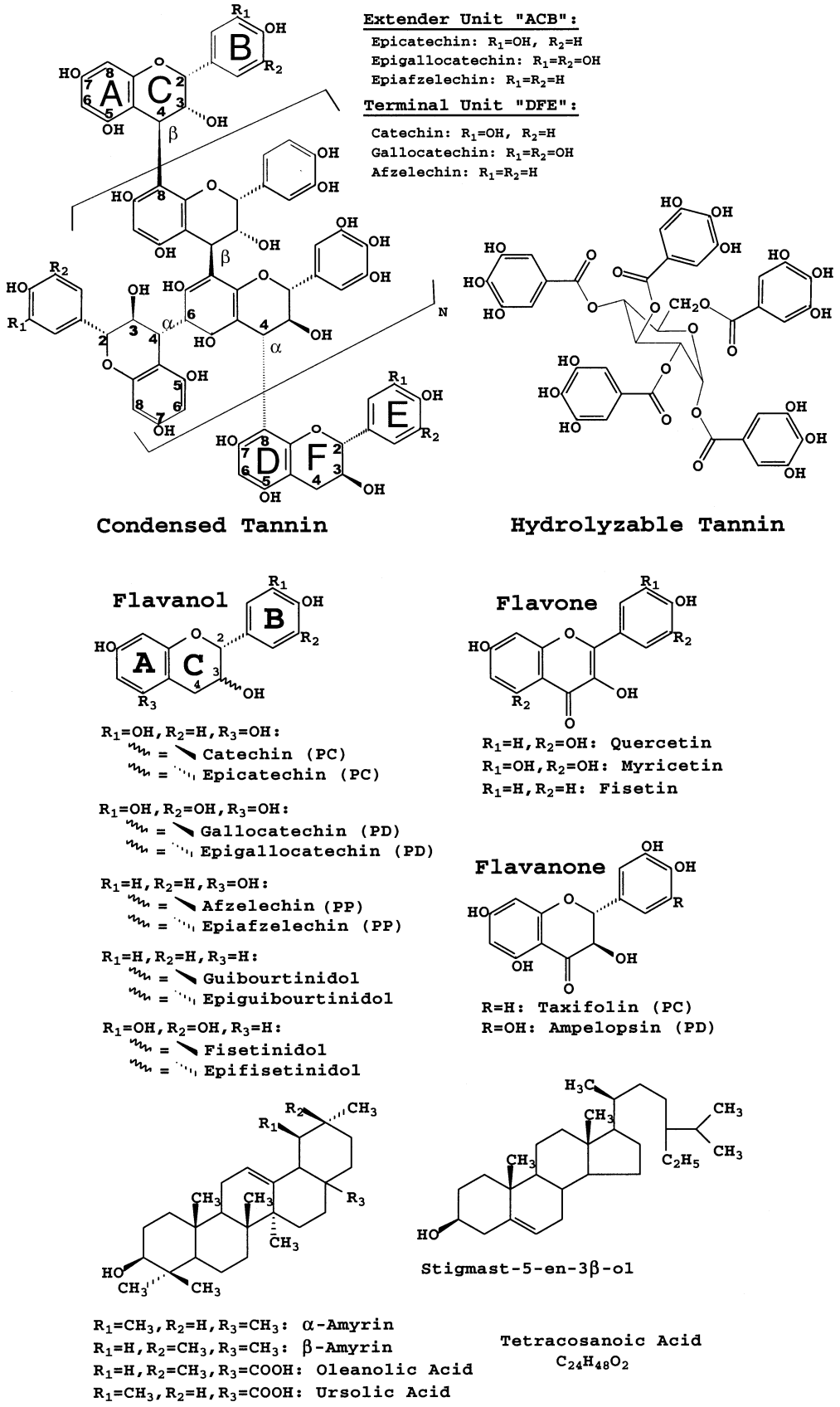


Fig. 1. Structures of typical condensed and hydrolyzable tannins, along with underivatized phenols, triterpenols, and sterols measured in this study.

2. EXPERIMENTAL SECTION

2.1. Sample Collection and Preparation

Samples were obtained from a variety of sources. All temperate samples (including ferns, conifers, monocotyledons, and dicotyledons) were collected in Washington state. Green leaf samples for *Camellia* sp., *Malus* sp., *Rosa* sp., *Rubus* sp., *Quercus palustris*, and *Tsuga heterophylla* cones and bark were gathered in Seattle, WA. Monocotyledons were obtained around Dabob Bay, WA as described in Cowie and Hedges (1984). Some conifer species were also collected near Dabob Bay, WA as described by Hedges and Weliky (1989). The remainder of the temperate samples were found in the University of Washington main campus or arboretum as described in Goñi and Hedges (1990). All the Amazon samples (whole monocotyledons, green dicotyledon tree leaves, dicotyledon wood and bark) were collected in the Amazon River basin and identified as described in Hedges et al. (1986). All samples were oven-dried at 50–60 °C or freeze-dried and ground to pass a 42-mesh (350-μm) sieve.

2.2. Analytical Procedure

The analytical procedure used relies on acid depolymerization of the condensed tannin polymer. The cleavage products include intact terminal units and C-4 carbocation extender units (see structure in Fig. 1 for terminology). The latter must be captured by a nucleophile, in this case, phloroglucinol. A complete description of the tannin analytical procedure can be found in Hernes and Hedges (2000). Briefly, ~50 mg of plant material (12–24 samples at a time are routinely analyzed) was depolymerized in a 1.0 mol/L HCl, 0.26 mol/L phloroglucinol solution of acetone:water (70:30 v/v), total volume 3 mL. Sample tubes each contained a magnetic stir bar, and the reaction was carried out in a constant temperature bath (30°C) for 24 h over a magnetic stir plate. Upon completion of the depolymerization, 100–150 μg of internal standard, hematoxylin, was added. The reaction mixture was then diluted with 10 mL water, and extracted 3× with ethyl acetate. After passing through anhydrous Na_2SO_4 drying columns to remove water, the ethyl acetate solution was split (two-thirds for archive, one-third for analysis), dried under a stream of N_2, and the samples placed in a vacuum dessicator overnight. The next morning, the one-third split was redissolved in 200 μL pyridine. A subsample (20–30 μL) was placed in an autosampler vial (containing a 200-μL insert) along with an equal volume of Regisil, (bis(trimethylsilyl)trifluoroacetamide) + 1% trimethylchlorosilane (Regis Chemical Co.), and heated to 60°C for 15 min to produce trimethylsilyl (TMS) derivatives.

All samples were analyzed using a Shimadzu AOC-14 autoinjector coupled to a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector (FID). Peak identification was done with a Hewlett-Packard 5970 Mass Selective Detector. Analyses were made by using splitless injection on a 30 m by 0.25 mm i.d. fused-silica capillary column coated with DB35ms liquid phase (J&W Scientific Inc.). The oven temperature was held at 70°C for 2 min during column loading, then increased to 200°C at 25°C/min. A second ramp of 4°C/min increased the oven temperature to 330°C which was maintained for 30 min. Electronic pressure control was also used during FID detection, with an initial column head pressure of 13 psi held for 2 min and then increased to 30 psi at 1 psi/min. A typical chromatographic trace of TMS-derivatized compounds is shown in Figure 2 for senescent *Rhizophora mangle* leaves. Underivatized compound structures of identified peaks are shown in Figure 1. Quantification was achieved using the internal standard and relative response factors determined from standard injections. When this research was conducted, commercially available standards included catechin, epicatechin, epigallocatechin, fisetin, quercetin, myricetin, taxifolin (dihydroquercetin), ampelopsin (dihydromyricetin), oleanolic acid, and ursolic acid. For compounds with no available standards (primarily the phloroglucinol adducts), the response of the internal standard was used.

3. RESULTS AND DISCUSSION

A challenge in any study involving tannin is that this macromolecular material "resists" broad taxonomic classification. There are well over 4000 unique flavanoid structures that have been isolated and identified in the literature (Harborne et al., 1975). Given the many different biochemical and ecological functions ascribed to tannins and polyphenols (Appel, 1993 and references therein), this molecular diversity is not surprising. The number of flavanoids incorporated into condensed tannin is considerably smaller, but the overall diversity (combined with multiple functions) means that individual species can have quite different tannin suites. Thus, there is great potential for distinguishing individual source contributions in a variety of natural settings. Nevertheless, if any condensed tannin is present in a sample, there is a great likelihood that a component of it will be procyanidins (PC) in the form of catechin and epicatechin (Harborne et al., 1975; Haslam, 1989). For instance, of the 117 samples analyzed in this study, 89 contained tannin, and 88 of those contained at least one PC tannin. In comparison, 50 contained prodelphinidin (PD) tannin in the form of gallocatechin and epigallocatechin, and 24 contained propelargonidin (PP) tannin in the form of afzelechin and epiafzelechin. In addition, 22 samples contained flavones (i.e., flavanols with a 2,3 double bond and a carbonyl at C-4), and six had flavanones (i.e., flavanols with a carbonyl at C-4. See Fig. 1 for structural differences). The complete molecular data set can be found in the Appendix. Commonly measured parameters for all samples are found in Table 1. Because flavanones are believed to occur as terminal units in condensed tannin, they were included in PC and PD totals as indicated in Figure 1 and Table 1.

As mentioned previously, a number of triterpenoids and sterols also fall within the analytical window of the method. The predominant sterol, stigmast-5-en-3β-ol (synonyms β-sitosterol and 24-ethylcholesterol), was present in 94 of the samples. Stigmast-5-en-3β-ol is one of a class of steroids that are widespread in angiosperms, gymnosperms, and ferns (Gershenzon and Croteau, 1991) and is also present in marine sources (Volkman, 1986). The primary diagnostic triterpenoids are the amyrins, which were present in 27 of the samples, and oleanolic and ursolic acids, at least one of which was present in 17 samples. The amyrins as well as oleanolic and ursolic acids are uniquely terrestrial, widespread in angiosperms, and are thought to be bonded to carbohydrates (Gershenzon and Cro-

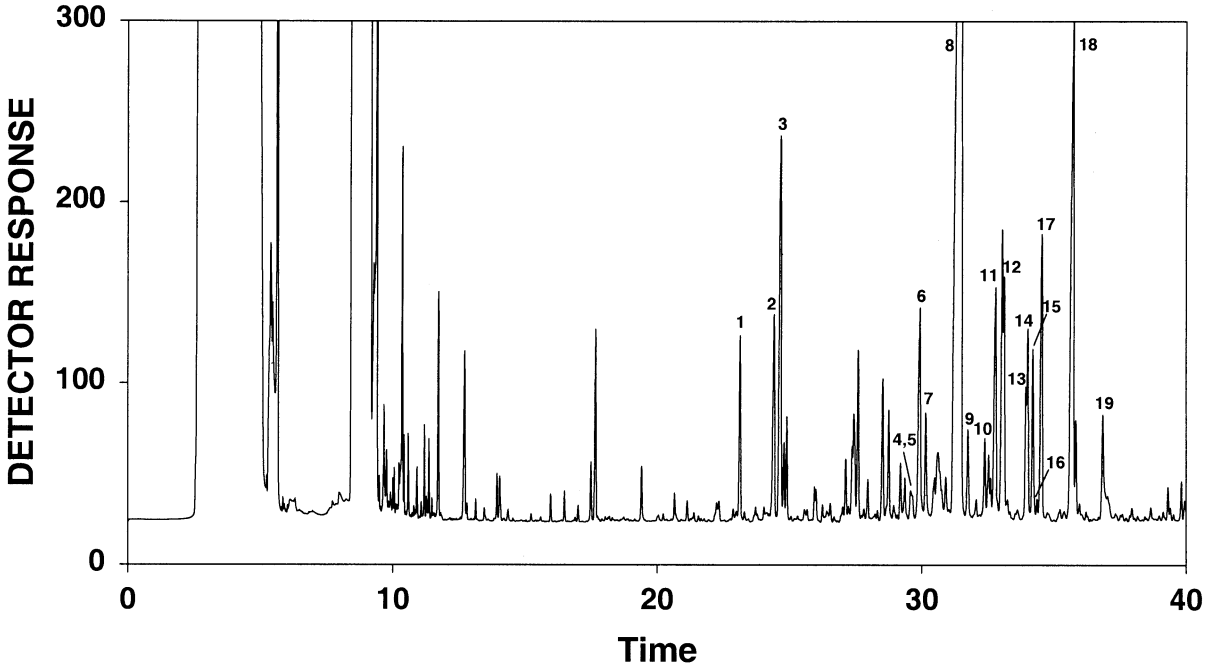


Fig. 2. GC trace of *Rhizophora mangle* yellow leaves, all compounds TMS-derivatized. 1 = hematoxylin; 2 = epicatechin; 3 = catechin; 4 = epigallocatechin; 5 = gallocatechin; 6 = quercetin; 7 = myricetin; 8 = epicatechin-(4α→2)-phloroglucinol; 9 = catechin-(4β→2)-phloroglucinol; 10 = stigmast-5-en-3β-ol; 11 = taraxerol; 12 = β-amyrin; 13 = epicatechin-(4β→2)-phloroglucinol; 14 = α-amyrin; 15 = catechin-(4α→2)-phloroglucinol; 16 = epigallocatechin-(4α→2)-phloroglucinol; 17 = epicatechin-derivative-(4→2)-phloroglucinol; 18 = gallocatechin-(4β→2)-phloroglucinol; 19 = epicatechin-derivative-(4→2)-phloroglucinol.

teau, 1991). Although not definitively known, their function is believed to be similar to many of the polyphenols, i.e., for defense against herbivores.

Additional compound types that fall within the analytical window include carboxylic acids (tetracosanoic acid was quantified in this study), carbohydrates, and gallic acid. The latter may be derived from hydrolysable tannin, but in general this method does not appear to be efficient for hydrolysable tannin.

There are a number of valid ways in which the analyzed samples can be grouped for comparison and source distinction, e.g., tropical vs. temperate, woody vs. nonwoody, angiosperm vs. gymnosperm. For the purposes of discussion, we chose to group them according to tissue types.

3.1. Bark

The molecular contribution of bark to carbon cycling is not well known. Our data set certainly represents one of the largest characterizations to date of this tissue type. A number of trends stand out in our measured molecular compositions (Table 1, Appendix). Perhaps the most noteworthy is the unique presence of measurable flavanones in the three conifers, *Pinus contorta* (0.58 wt.% dihydroquercetin or taxifolin, 1.25 wt.% dihydromyricetin or ampelopsin), *Pinus ponderosa* (0.60 wt.% taxifolin), and *Pseudotsuga menziensii* (2.28 wt.% taxifolin). Bark flavanones are believed to occur in condensed tannin (Hergert, 1989), but because of the carbonyl function on C-4, can only be present as terminal units.

Quantitatively, *Tsuga heterophylla* bark yielded nearly 10.6 wt.% tannin phenols, whereas total tannin yields from the other 17 samples ranged from undetectable (three samples) to 3.1 wt.%. Tannin yields from conifer barks tended to be higher than from barks of either the tropical or temperate dicotyledons. Although PC tannin was the most common flavanol found in the barks, once again individual species exhibit substantial variation. *Tsuga heterophylla* bark showed the highest yield (>3%) of PP tannin of any samples in the entire data set, whereas bark of the tropical dicotyledon, *Neoxythece elegans*, yielded nearly 90% PD tannin. *Neoxythece elegans* also showed the highest degree of polymerization (total tannin divided by total terminal units—a measure of average tannin chain length) with a chain length of 11. Degree of polymerization by itself is not likely to provide much source information, but can reflect degradation downstream of the source. On average, however, the measured barks of tropical dicotyledons showed a higher degree of polymerization (1.7 to 11) than the conifer barks (1.2–4.4). Finally, *Pinus contorta* and *Quercus garrayana* yielded small amounts of flavones. Hergert (1989) also reported their presence in the barks of *Tsuga heterophylla* and *Picea sitchensis*.

Other than stigmast-5-en-3β-ol, triterpenoids were not found in any of the conifers. On the other hand, many were measured in the angiosperms. Again, *Neoxythece elegans* stands out with 1.1 wt.% each of α- and β-amyrin, and 0.84 wt.% of oleanolic acid. In addition, *Alnus rubra* and *Zanthoxylum compactom* yielded roughly 1 and 2 wt.%, respectively, of a compound with a mass spectrum similar to the amyrins, but with an additional 131 *m/z* fragment. The only other tissue in the entire sample set yielding a similar product was *Alnus rubra* seed

Table 1. Tannin and triterpenoid parameters.

Latin name	LBL	TISS.	ΣTannin Wt.%	Xn	Terminal *cis/trans*	Extender *cis/trans*	PC:PD:PP	ΣTerp. Wt.%
Acer macrophyllum	d	BK	0.09	2.57	1.00	0.78	100:0:0	
Alnus rubra	d	BK	0.49	2.49	0.49	0.88	93:7:0	1.25
Artemisa tridentata	d	BK					::	
Quercus garrayana	d	BK	0.47	1.39	0.13	0.61	88:12:0	0.10
Thuja plicata	gc	BK	1.48	2.44	0.28	0.22	80:3:17	
Abies holophylla	gp	BK	0.20	1.17	0.46	1.00	100:0:0	
Pinus contorta	gp	BK	2.97	4.38	0.08	0.60	66:34:0	
Pinus ponderosa	gp	BK	2.15	2.37	0.11	0.74	97:3:0	
Pseudotsuga menziensii	gp	BK	3.11	2.50	0.56	0.64	100:0:0	
Tsuga heterophylla	gp	BK	10.57	1.42	0.56	0.68	69:2:28	
Aniba guianensis	td	BK	0.48	2.09	0.42	0.79	100:0:0	
Clarisia racemosa	td	BK	0.06	2.60	0.90	0.68	27:0:73	0.88
Crescentia amazonica	td	BK					::	
Genipa americana	td	BK	0.00	1.00	1.00		100:0:0	0.01
Nectandra amazonium	td	BK	1.33	2.52	0.56	0.83	98:2:0	
Neoxythece elegans	td	BK	0.65	10.91	0.29	0.36	14:86:0	3.21
Xylosma intermedium	td	BK	0.05	1.71	0.00	0.64	89:11:0	0.03
Zanthoxylum compactum	td	BK					::	2.00
Larix occidentalis	gp	C	0.87	5.35	0.25	0.85	97:3:0	
Picea sitchensis	gp	C	0.30	1.82	0.08	0.64	75:25:0	
Pinus ponderosa	gp	C	0.66	2.39	0.06	0.62	100:0:0	
Pseudotsuga menziensii	gp	C	2.00	5.00	0.54	0.90	100:0:0	
Tsuga heterophylla	gp	C	3.13	7.37	0.23	0.39	38:61:0	
Sequoia sempervirens	gT	C	1.81	5.15	0.32	0.37	32:68:0	
Alnus rubra	d	S	1.87	5.25	0.80	0.93	100:0:0	4.53
Acer macrophyllum	d	GL	0.63	2.22	0.25	0.75	77:23:0	0.23
Alnus rubra	d	GL	0.96	2.97	0.53	0.87	95:5:0	0.36
Artemisa tridentata	d	GL					::	
Avicennia germinans	d	GL					::	
Camellia spp.	d	GL	3.72	1.46	0.80	0.52	100:0:0	0.03
Ilex aquifolium	d	GL	0.03	1.24	1.00	1.00	100:0:0	3.40
Malus spp.	d	GL	0.89	6.99	0.82	1.00	59:0:41	1.10
Populus trichocarpa	d	GL	2.13	5.32	0.04	0.65	77:23:0	
Quercus garrayana	d	GL	2.22	1.74	0.41	0.66	84:16:0	0.20
Quercus palustris	d	GL	0.59	1.67	0.00	0.84	100:0:0	0.74
Quercus robur	d	GL	0.44	1.81	0.00	0.75	92:8:0	0.09
Quercus rubra	d	GL	0.64	1.74	1.00	0.93	100:0:0	0.40
Rosa spp.	d	GL	1.70	1.99	0.10	0.84	98:2:0	0.11
Rubus spp.	d	GL	0.09	1.27	1.00	1.00	100:0:0	
Vitis spp.	d	GL	4.67	4.28	0.55	0.52	49:51:0	
Aniba guianensis	td	GL	0.59	2.65	0.48	0.94	100:0:0	
Aspidosperma rigida	td	GL					::	
Bothriospora lorymbosa	td	GL	0.17			1.00	100:0:0	0.08
Buchenavia oxycarpa	td	GL	0.02			0.61	61:39:0	0.10
Campsiandra comosa	td	GL	1.33	1.58	0.29	0.76	70:4:6	
Caraipa grandifolia	td	GL	0.70	3.05	0.82	0.87	91:9:0	0.18
Clarisia racemosa	td	GL	1.61	3.70	0.50	0.90	37:0:63	0.20
Genipa americana	td	GL	0.09	1.43	0.66	1.00	100:0:0	1.55
Glycydendron amazonicum	td	GL	1.19	10.66	0.00	0.50	43:56:1	
Guarea rubiflora	td	GL	1.30	5.32	0.73	0.56	55:45:0	0.06
Guarea trichilioides	td	GL	1.53	3.32	0.47	0.80	99:1:0	
Lecointea amazonica	td	GL	0.03			0.88	88:12:0	0.14
Leonia racemosa	td	GL					::	
Malouetia furfuracea	td	GL	2.09	3.10	0.56	0.74	41:5:54	2.74
Nectandra amazonium	td	GL	0.63	2.79	0.53	0.98	100:0:0	
Neoxythece elegans	td	GL	1.13	3.60	0.56	0.17	18:82:0	0.20
Pterocarpus amazonicus	td	GL	0.52	6.29	0.76	0.37	30:70:0	0.06
Rhizophora mangle	td	GL	5.23	7.33	0.28	0.79	87:13:0	0.06
Symmeria paniculata	td	GL	1.57	2.55	0.91	0.97	99:0:1	
Tabebuia barbata	td	GL					::	1.86
Vatairea guianensis	td	GL	0.37	1.53	0.07	1.00	36:0:64	0.16
Vitex cymosa	td	GL					::	0.90
Xylopia callophylla	td	GL	1.38	3.56	0.82	0.98	100:0:0	
Xylosma intermedium	td	GL	0.28	1.79	0.11	0.83	100:0:0	0.05
Zanthoxylum compactum	td	GL	0.99	2.88	0.69	0.99	100:0:0	

Table 1. (Continued)

Latin name	LBL	TISS.	ΣTannin Wt.%	Xn	Terminal *cis/trans*	Extender *cis/trans*	PC:PD:PP	ΣTerp. Wt.%
Araucaria araucana	ga	GN	2.49	5.08	0.28	0.48	45:51:5	
Thuja plicata	gc	GN	5.05	3.22	0.22	0.56	43:55:3	
Abies marocana	gp	BN	6.02	2.72	0.14	0.42	42:57:1	
Abies nebrodensis	gp	BN	6.20	2.82	0.07	0.36	34:66:0	
Picea engelmannii	gp	GN	2.35	3.53	0.16	0.74	82:18:0	
Picea sitchensis	gp	BN	1.36	3.00	0.20	0.95	98:1:0	
Pinus contorta	gp	GN	10.06	4.53	0.07	0.35	26:73:1	
Pinus ponderosa	gp	GN	8.63	5.69	0.08	0.26	27:73:1	
Pseudotsuga menziensii	gp	GN	5.61	7.82	0.42	0.45	45:54:1	
Tsuga heterophylla	gp	GN	4.63	12.82	0.32	0.30	27:73:0	
Sequoia sempervirens	gT	GN	5.49	7.04	0.19	0.33	27:73:0	
Sequoiadendron giganteum	gT	GN	2.77	6.45	0.20	0.44	43:57:0	
Taxodium distichum	gT	GN	4.23	6.95	0.14	0.45	43:57:0	
Taxodium distichum	gT	GN	2.77	7.42	0.14	0.45	46:54:0	
Alnus rubra	d	W	0.61	2.31	0.06	0.77	92:8:0	
Thuja plicata	gc	W					::	
Picea sitchensis	gp	W	0.01			1.00	100:0:0	
Picea spp.	gp	W	0.01			1.00	100:0:0	
Pseudotsuga menziensii	gp	W	0.01				::	
Bothriospora lorymbosa	td	W					::	0.14
Buchenavia oxycarpa	td	W					::	
Campsiandra comosa	td	W	0.41	1.75	0.09	0.67	74:0:0	
Clarisia racemosa	td	W					::	
Leonia racemosa	td	W					::	
Neoxythece elegans	td	W	0.01	3.97	1.00	0.32	49:51:0	
Symmeria paniculata	td	W	0.60	1.80	0.55	0.94	100:0:0	
Tabebuia barbata	td	W					::	
Vitex cymosa	td	W					::	
Xylopia callophylla	td	W					::	
Xylosma intermedium	td	W	0.03	4.43	1.00	1.00	100:0:0	
Rhacomitrium aciculare	B	WP					::	
Rhytidiadelphus loreus	B	WP					::	
Lycopodium sitchense	C	WP	0.02			1.00	100:0:0	
Polystichum acrostichoides	F	WP	1.09	6.84	0.78	0.93	86:8:6	
Pteridium aquilinium	F	WP	0.93	7.75	1.00	0.73	63:30:7	
Equisetum telmateia	H	WP	1.24	37.10	0.85	1.00	58:0:42	
Alaria fistulosa	K	B					::	
Alaria fistulosa	K	ST					::	
Laminaria longpipes	K	WP					::	
Thalasiophylum	K	WP					::	
Agrostis alba	m	WP	0.02			0.21	21:79:0	
Avena spp.	m	WP					::	
Carex spp.	m	WP					::	
Salicornia spp.	m	WP					::	0.12
Spartina alterniflora	m	WP					::	0.10
Zostera spp.	m	WP					::	
Echinochloa polystachya	tm	WP	0.00			1.00	100:0:0	
Eichomia crassipes	tm	WP	0.42	6.74	1.00	1.00	67:0:33	
Gynerium sagittatum	tm	WP	0.01	2.20	0.00	0.00	100:0:0	
Paspalum repens	tm	WP	0.03	1.91	1.00	1.00	100:0:0	
Pistia stratoides	tm	WP	0.01			1.00	100:0:0	
Salvinia auriculata	tm	WP	1.46	11.28	1.00	0.99	91:0:9	

Abbreviations: LBL = plant type; TISS. = tissue type; ΣTannin = total molecular tannin; Xn = degree of polymerization; *cis/trans* = fraction of 2,3 bond in the *cis* conformation; PC = procyanidin (epicatechin + catechin + taxifolin); PD = prodelphinidin (epigallocatechin + gallocatechin + ampelopsin); PP = propelargonidin (epiafzelechin + afzelechin); ΣTerp. = total triterpenoids.

Plant types: d = temperate dicotyledons; td = tropical dicotyledons; ga = gymnosperms family Araucariaceae; gc = gym. f. Cuppresaceae; gp = gym. f. Pinaceae; gT = gym. f. Taxodiaceae; B = mosses; C = club mosses; F = ferns; H = horsetails; K = kelps; m = temperate monocotyledons; tm = tropical monocotyledons.

Tissue types: BK = bark; C = cone; S = seedpod; GL = green leaves; GN = green needles; BN = brown needles; WP = whole plant; W = wood; B = blade; ST = stipe.

pods, indicating a potentially unique marker for *Alnus rubra* tissues. In general, barks were elevated in carboxylic acids. Most were not quantified, except for tetracosanoic acid, which again was detected only in bark tissues, namely the angiosperm, *Alnus rubra*, in trace amounts (0.03 wt.%), and the conifers *Abies holophylla*, *Pinus contorta*, and *Pinus ponderosa* in greater amounts (~0.25 wt.%).

Two of the barks in our sample set (*Pinus contorta* and *Pseudotsuga menziensii)* have been previously analyzed by a molecular acid thiolysis method (Matthews et al., 1997b). Whereas Matthews et al. (1997b) measured 3.2% and 3.3% of total PC plus PD tannin, we obtained 3.0% and 3.1%, respectively (Table 1). Part of this close agreement may be fortuitous, however, since our analysis also includes flavanones, which constitute about half the tannin measured in these two samples. Degree of polymerization was higher in their samples: 4.7 and 3.7, respectively, vs. 4.4 and 2.5. Compositionally, Matthews et al. (1997b) found a 60:40 and 81:19% ratio of 2,3-*cis* (i.e., the epi- forms epicatechin, epigallocatechin, and epiafzelechin—monomer "ACB" in Fig. 1) to 2,3-*trans* (catechin, gallocatechin, and afzelechin—monomer "DFE" in Fig. 1) conformations, respectively, whereas our ratios were 60:40 and 64:36. These authors found <20% of the condensed tannin in *Pinus contorta* bark was of PD type, as compared to a previous literature value of 69% (Porter, 1989). Our measurement of 34% PD tannin falls in between these values. No PD tannin was measured in *Pseudotsuga menziensii* bark in either study. Finally, our analysis of *Tsuga heterophylla* bark yielded 10.6% tannin vs. a value of 12.6% reported by Hergert (1989).

3.2. Cones and Seedpods

Tannin yields from six seed cones and one angiosperm seed pod (*Alnus rubra*) ranged from 0.3 to 3.1 wt.%. Compositionally, the only distinguishing feature was the presence of triterpenoids in *Alnus rubra* tissues and their absence in all of the conifers—a pattern similar to what was found in the barks. In addition to the "131-amyrin" noted above, the *Alnus rubra* seed pods yielded more than 4% of an unidentified triterpenoid with a prominent 587 *m*/*z* fragment. The only other plant tissue in the entire sample set giving a similar compound was *Alnus rubra* green leaves. Given the 587 peak in *Alnus rubra* seedpods and green leaves combined with the "131-amyrin" in seedpods and barks, red alder sources should be readily discernable in natural environments.

Our results on the seed cones can be compared to the study of Eberhardt and Young (1994), who analyzed purified condensed tannins from five *Pinus* spp. seed cones with ^{13}C-NMR spectroscopy. They found that 2,3-*cis* conformations made up 65–81% of condensed tannin. Our results are in good agreement, with 2,3-*cis* constituting 62–90% in four species from the *Pinaceae* family, and 37% and 39% in *Sequoia sempervirens* and *Tsuga heterophylla*, respectively. The only common species between the two sets of seed cones was *Pinus ponderosa*, in which they measured 74% 2,3-*cis* vs. 62% in this study. The degree of polymerization ranged from 5.3–8.5 in Eberhardt and Young's study, and from 1.8–7.4 in this study (5.4 vs. 2.4 for *Pinus ponderosa*). This difference may be explained by the fact that the purification procedure employed by Eberhardt and Young eliminates monomers and smaller oligomers. None of the seed cones from *Pinus* spp. measured in either study contained any PD tannin. However, we found >60% PD tannin in cones of *Sequoia sempervirens* and *Tsuga heterophylla*. The latter is interesting, because of the contrast with *Tsuga heterophylla* bark which contained only 3% PD tannin. As in the bark, *Pseudotsuga menziensii* seed cones, as well as *Alnus rubra* seed pods, contained no PD tannin.

3.3. Conifer Needles

Total tannin in the conifer needles ranged from 1.4 wt.% to 10.0 wt.%, with half greater than 5% and the two *Picea* spp. giving the lowest values. The 10.0% value was measured in *Pinus contorta*, 8.6% in *Pinus ponderosa*, while *Pseudotsuga menziensii* was 5.6%. In addition to distinct signatures, the abundance of tannin in conifer needles could have a measurable impact on litters and soils.

Of the 14 needles analyzed, 12 were virtually identical compositionally, the only exceptions being the two *Picea* spp. Among the 12, the percent of PD tannin ranged from 54–74%. Among temperate species, conifer needles were the only tissues to exhibit >23% PD, with the exception of *Vitis* spp. green leaves (51%), and the bracken fern *Pteridium aquilinium* (33%). Thus, PD tannin might be a useful marker of conifer needles. In 13 of the species, gallocatechin ranged from 70–100% of the PD tannin. Gallocatechin was predominant in nearly all tissues that contained PD tannin. In all needle samples, the percent catechin of PC tannin ranged from 8% to 21%. This composition is consistent with results for conifer seed cones and barks. Finally, eight of the needle samples yielded measurable PP tannin. Among temperate nonconifer species analyzed, PP was found in only one angiosperm (*Malus* spp.), both ferns, and the single horsetail (Table 1). Thus, PP may also be useful as an indicator of conifer needles.

Degree of polymerization in conifer needle tannin ranged from 2.7–12.8, the latter in *Tsuga heterophylla*. Values are generally comparable to that for conifer seed cones, but at least a factor of two greater than that in conifer barks.

3.4. Dicotyledon Leaves

Leaves were analyzed from 15 temperate and 25 tropical dicotyledons. In all, 13 of the temperate and 21 of the tropical species contained tannin. All tropical leaves yielded less than 2.1 wt.% total tannin except for *Rhizophora mangle* (5.2 wt.%), whereas four temperate leaves gave yields higher than 2.1 wt.%, including *Vitis* spp. (4.7%) and *Camellia* spp. (3.7%). In contrast to conifer needles, 25 of the dicotyledon leaves yielded triterpenoids, with total yields as high as 3.4 wt.% in *Ilex aquifolium*.

Compositionally, there were some differences between leaves from the tropical and temperate dicotyledons. Whereas 10 of 15 temperate species contained quercetin (as high as 1.6 wt.% in *Malus* spp.), it was measured in only six of 25 tropical species. Leaves from five tropical species gave PP tannin, compared to only one temperate. Tropical species were more likely to yield high proportions of PD tannin relative to total tannin, with five species ranging from 39–82% PD. Only one temperate leaf yielded greater than 23% PD tannin. In both temperate and tropical leaves, epicatechin was the primary

extender unit, similar to what is reported in the literature (e.g., Harborne et al., 1975; Haslam, 1989).

One of the more intriguing leaf samples is from the tropical species, *Campsiandra comosa*, which was the only species in the entire sample set that contained proguibourtinidin or profisetinidin tannin (i.e., with only one hydroxyl group on the A-ring—see Fig. 1). Such tannins are comparatively rare, and reportedly more resistant to acid depolymerization when present as extender units (Patil and Deshpande, 1982; Steenkamp et al., 1985). Because these compounds were only found in the extender units, the 0.27 wt.% yield from *Campsiandra comosa* might be indicative of considerably more precursor in the leaf.

Leaves from six species of dicotyledons contained compounds corresponding to hydroxyoleanolic and hydroxyursolic acid. The position of the hydroxy group on the triterpenoid structures could not be determined by mass spectra alone. In five of the six leaves, the parent compounds, oleanolic and ursolic acid, were also present.

Finally, two compounds corresponding to amyrins with the addition of a methyl group were detected in leaves of two tropical species, *Clarisia racemosa* and *Malouetia furfuracea.* One of the compounds was also detected in *Clarisia racemosa* bark. Notably, these two species also contained >1 wt.% PP tannin, which was more than half the tannin present in these samples. *Vatairea guianensis* was the only other tropical species to yield more than 6% PP of the total tannin.

3.5. Monocotyledons

Whole plants from six species each of temperate and tropical monocotyledons were analyzed. All tropical monocots yielded some tannin, ranging from <0.01 wt.% up to 1.46%. Two of the six species yielded PP tannin, whereas none yielded PD tannin. Only one temperate grass, *Agrostis alba*, yielded measurable tannin (0.02 wt.%), and was also the only monocotyledon to yield PD tannin. *Zostera* spp. have been shown to have phenolic content as measured by Folin-Denis reagent (Harrison and Durance, 1989), but similar to McMillan (1984), we found no condensed tannin. Molecular data for the tropical water hyacinth *Eichornia crassipes* can be found in Ellis et al. (1983). Whereas they report PC:PD:PP ratios of 56:19:25, we measured 67:0:33. Ellis et al. found 2,3-*cis*/*trans* ratios in *Eichornia crassipes* of 40:60, while no *trans* was measured in this study.

Monocotyledons were distinct from the dicotyledons in that no triterpenoids were detected in the former, other than the ubiquitous stigmast-5en-3β-ol.

3.6. Woods

Only half of the 16 wood samples analyzed in this study contained measurable tannin. *Alnus rubra*, a temperate dicotyledon, and *Symmeria paniculata*, a tropical dicotyledon, each gave 0.6 wt.% tannin. *Campsiandra comosa* yielded 0.4% tannin, and all others were 0.03% or less. No compositional feature stands out for woods. Individually, *Campsiandra comosa* wood yielded proguibourtinidin and profisetinidin tannin, just as the leaves did. As in most tissues, the *cis* form of the tannin was generally more abundant than the *trans*.

3.7. Ferns, Horsetails, Kelps, Mosses, and Clubmosses

No tannin was measured in the three kelps and two mosses, and only 0.02 wt.% was measured in the single club moss, *Lycopodium sitchense*. On the other hand, the two ferns, *Polystichum acrostichoides* and *Pteridium aquilinium*, yielded ~1% tannin, and the horsetail, *Equisetum telmateia*, yielded 1.2% tannin. All three contained PP tannin, and both ferns contained PD tannin. All three tissues contained >90% of the *cis* form of tannin, and relatively high degrees of polymerization at 6.8, 7.8, and 37.1, respectively. Although compositional trends cannot be established on such a small sampling, it is clear that ferns and horsetails can be possible sources of tannin. In particular, the PD and PP tannin content might be mistaken as conifer in origin.

3.8. Parameters for Source Distinctions

All told, there are at least 18–20 different categories of plant materials represented by the 117 samples analyzed in this study, based on temperate vs. tropical habitats, taxonomic distinctions, and tissue type. As such, there is no universal parameter for distinguishing all of them in an unknown environmental sample such as soils or sediments on the basis of tannin composition alone. A more useful concept might be something akin to a dichotomous key, as is commonly used in biologic sciences to “type” organisms. In this sample set, the first key might be the geographic location of the sample, i.e., temperate vs. tropical since most species are not likely to be present in both settings. Further keys could be based on chemical composition parameters, including those presented here for tannin, triterpenoids, and other compounds, and those presented for the terrestrial counterparts cutin (Goñi and Hedges, 1990) and lignin monomers and dimers (Hedges and Mann, 1979; Goñi and Hedges, 1992).

Two types of parameters are generally used for source distinctions. The first denotes the presence of a specific compound (or compound class) unique to a subset of the source possibilities. Examples from this data set include (1) the flavanones, which were only measured in conifers and primarily in barks, (2) tetracosanoic acid in barks, (3) triterpenoids in angiosperms, and (4) PP tannin, which was only yielded by nonwoody tissues of conifers, tropical species, ferns, and horsetails. Given a comprehensive survey, these types of distinctions are robust in that one can generally infer the presence of the source from detection of the compound class. However, the converse is not always true, i.e., the absence of these compounds does not necessarily mean the absence of the sources.

The second type of parameter involves a compound (or compound class) that is present in all or most source types, but in varying compositional ratios. An example from this data set would be the fraction of 2,3-*cis* stereochemistry in the extender units of tannin. The presence of 2,3-*cis* extender units alone carries no source information, but in relation to 2,3-*trans* extender units, it carries a great deal. For instance, the fraction of 2,3-*cis* extender units is less than ~0.5 in all conifer needles analyzed except *Picea* spp. On the other hand, the fraction is greater than 0.5 from all tissue types in temperate or tropical angiosperms except the tropical dicotyledons *Neoxythece elegans* and *Pterocarpus amizonicus* and the temperate mono-

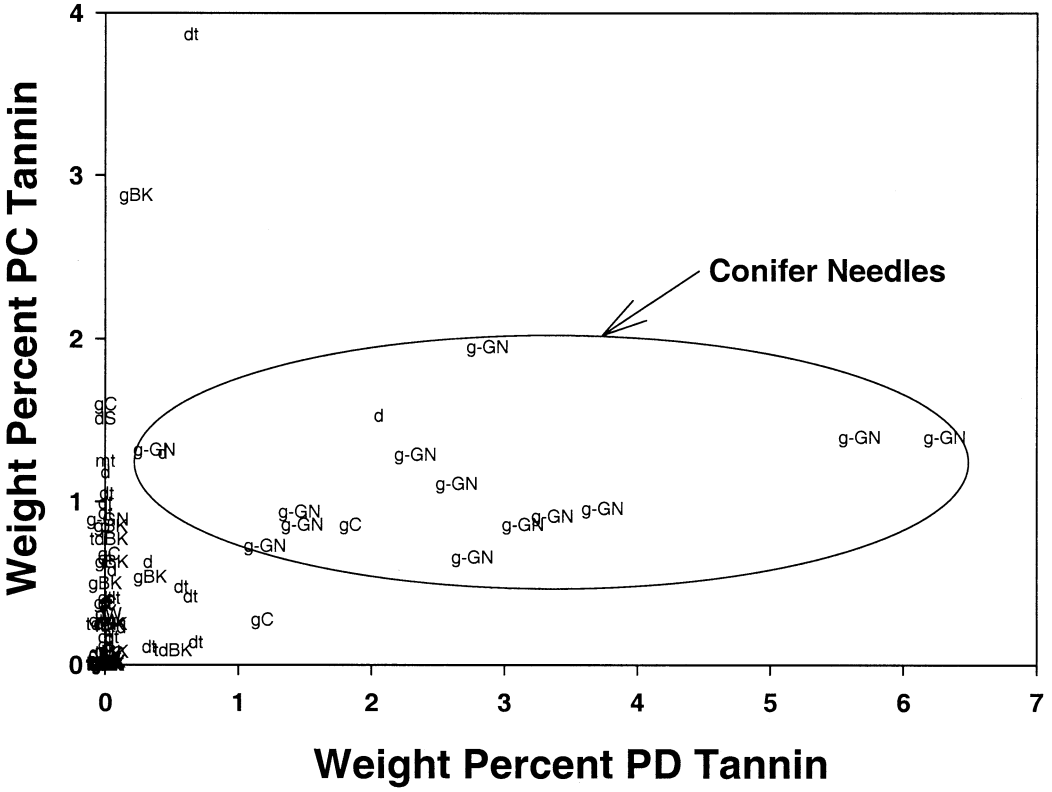


Fig. 3. Weight percent PC tannin vs. PD tannin for all samples.

cotyledon *Agrostis alba*. The latter, however, contained only 0.02 wt.% total tannin and would be essentially invisible in a tissue mixture.

Although the first type of unique biomarker can provide unambiguous evidence of a single source, abundance estimates of multiple sources are problematic unless there are unique markers for each endmember. The second type of parameter, on the other hand, lends itself readily to endmember mixing calculations because each endmember contributes to the bulk signal. In a gymnosperm/angiosperm mixture, for example, a measurement of 0.25 for the fraction of 2,3-*cis* extender units indicates both the predominance of gymnosperms and the absence of angiosperms. A value of 0.8 would indicate both the absence of gymnosperms and the predominance of angiosperms.

Although there are many examples of source-specific compounds of the first type, few span broad enough cross-sections of a category to be generally representative. For instance, flavanones, PP tannin, PG and PF tannin, tetracosanoic acid, the 587 peak and “131-amyrin” of *Alnus rubra*, hydroxyoleanolic and hydroxyursolic acid, and methyl amyrins all might be invaluable source markers in certain systems, but cannot be generalized to trace an entire tissue type. On the other hand, PD tannin, flavones, and total triterpenoids are found in enough species and tissue categories to warrant generalizations.

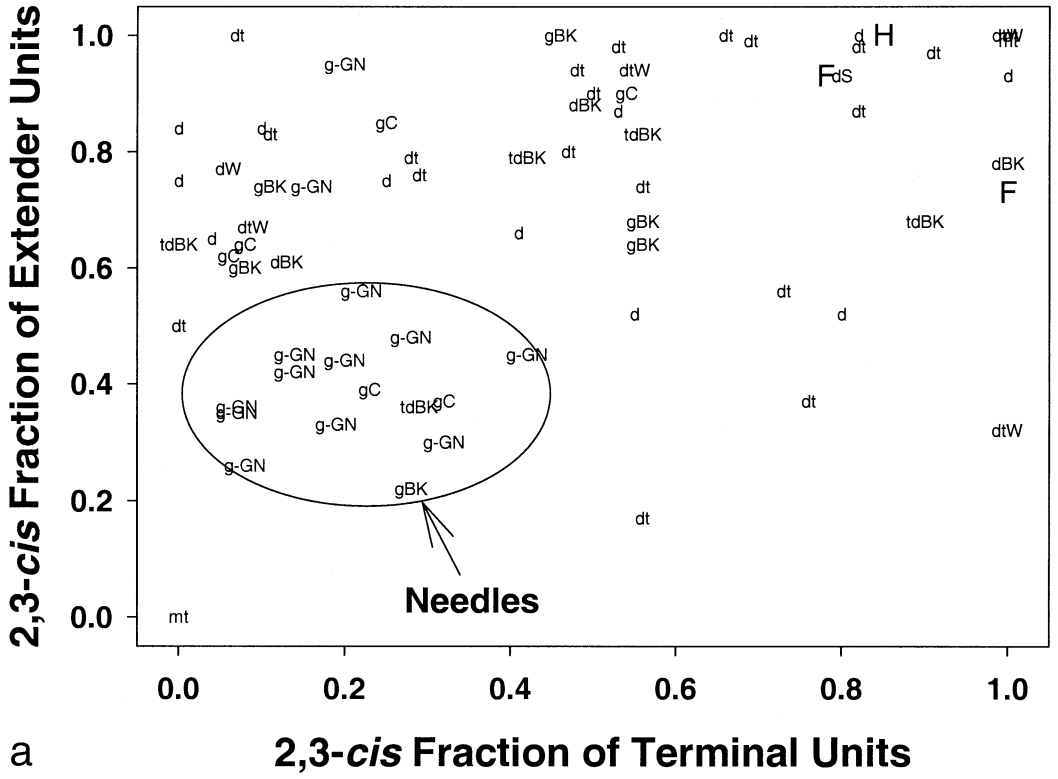
3.8.1. Parameters for Conifers

The primary reason that conifer needles yielded a lower fraction of 2,3-*cis* extender units is the presence of large amounts of PD tannin, which can be more than 90% *trans*. PD tannin yields obviously also directly impact PC:PD:PP percentages. Thus, conifers can be distinguished by any one of three parameters related to PD tannin: (1) weight percent PD tannin, which falls into the first category discussed above and only gives information about the presence of PD-bearing sources; (2) the fraction of 2,3-*cis* extender units; and (3) PC:PD:PP percentages, the latter two falling into the second category and giving information about all tannin-bearing sources. Although PD tannin is not exclusive to conifers, their tissues generally give the highest yields. A plot of weight percent PC vs. PD tannin illustrates this pattern (Fig. 3), in which conifer needles (except *Picea* spp.) are distinguishable from all other sources.

As discussed, the fraction of 2,3-*cis* extender units and PC:PD:PP percentages are closely related. When plotted against the fraction of 2,3-*cis* terminal units, either parameter is capable of differentiating conifer needles (less *Picea* spp.) from other tannin sources (Fig. 4a and 4b, respectively). PC:PD:PP, however, gives tighter clustering. Also of note is that ferns and horsetails (other sources of PD and PP tannin) are well removed from conifers on these plots, because their fractions of 2,3-*cis* terminal units are roughly double that of conifers.

3.8.2. Parameter for Leaves, Needles, and Barks

The abundances of flavones and triterpenoids could be similarly useful for distinctions between leaves, needles, and barks (Fig. 5). While there is considerable overlap between tropical and temperate dicotyledons, it is unlikely that both would be simultaneously present in natural samples. Also, only species



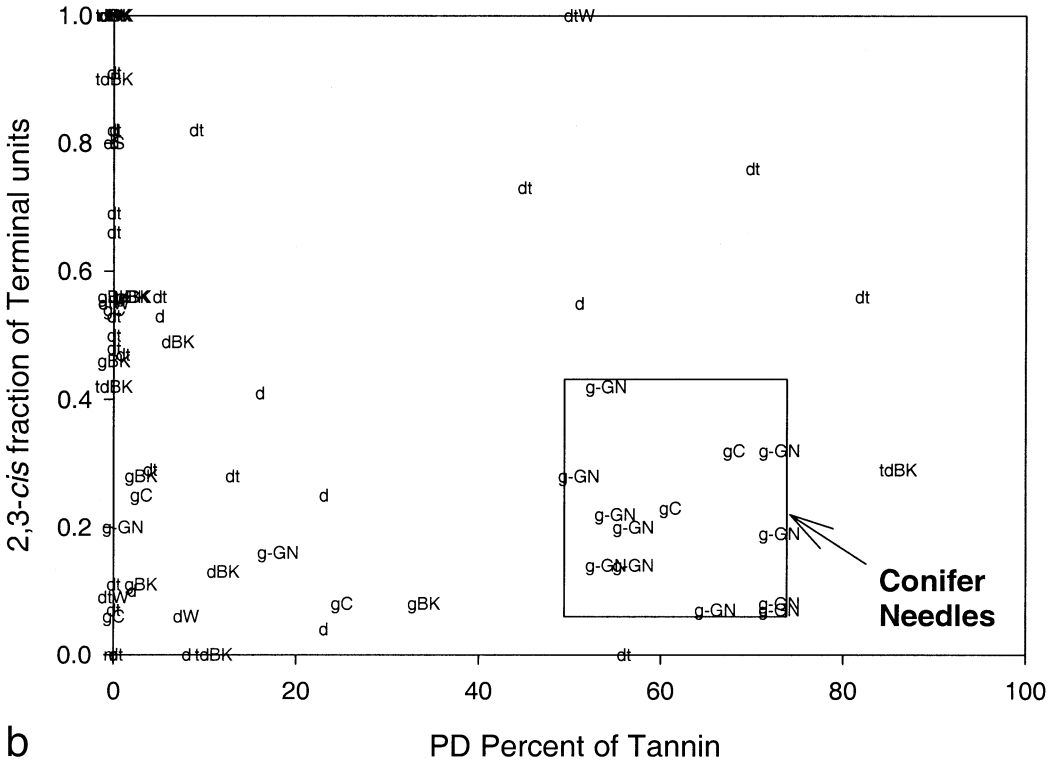


Fig. 4. (a) The fraction of 2,3-*cis* structures in extender vs. terminal units, and (b) the fraction of 2,3-*cis* terminal units vs. PD percent of tannin. Abbreviations are as in Table 1.

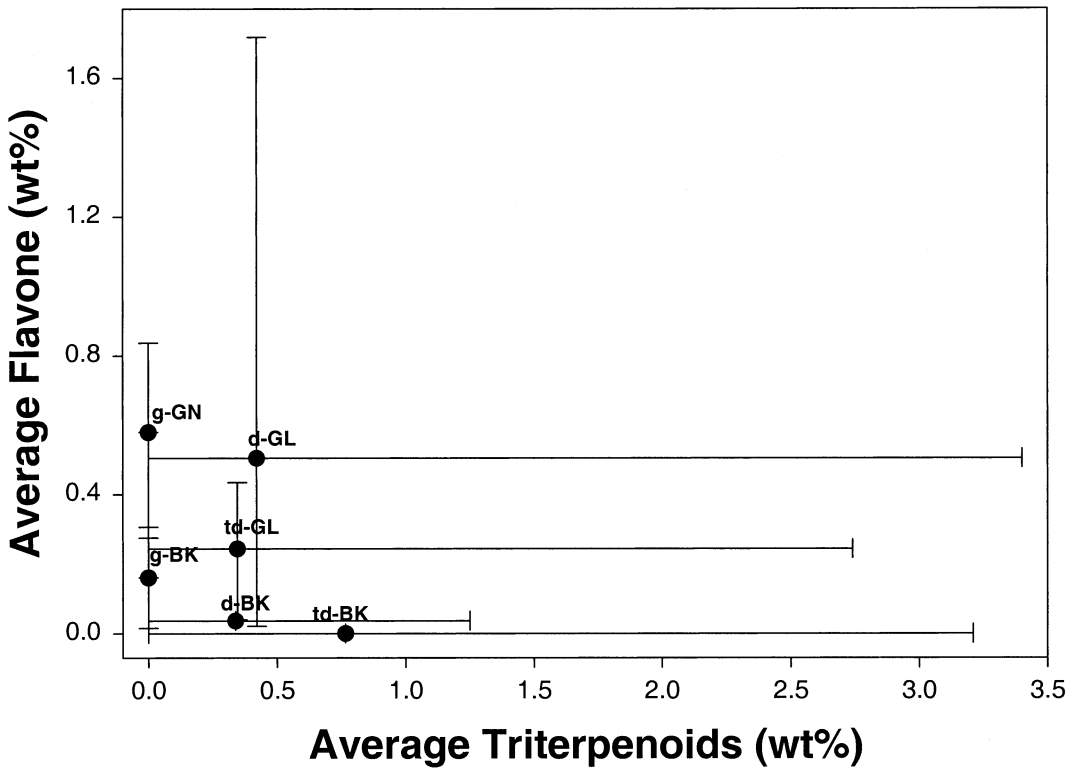


Fig. 5. Weight percent flavones vs. weight percent triterpenoids. Abbreviations are as in Table 1.

that yielded flavones and triterpenoids were included in these plots. Temperate dicotyledons contained flavones in a much higher percentage of species than any other category.

3.9. Diagenetic Effects

To fully evaluate the utility of these parameters, the effects of diagenesis must be considered. With all other factors equal, the extent of hydroxylation of the B-ring should parallel reactivity, with PD tannin more reactive than PC tannin (three vs. two vicinal hydroxyl groups prone to quinone formation), which in turn should be more reactive than PP tannin (only one hydroxyl group which will not form quinones). This inference appears to be the case for *Rhizophora mangle* (Hernes et al., 2001), but will be critical to evaluate in the case of conifers as the primary source of PD tannin. However, if the alteration products of the different tannin sources can eventually be identified and quantified, they could provide a powerful tool in the study of organic matter degradation. In a similar vein, degree of polymerization, while not particularly useful as a source indicator, could have utility in diagenetic studies because smaller compounds are generally more labile than larger counterparts. If so, plots of the fraction of 2,3-*cis* structures in terminal vs. extender units would be skewed toward the composition of extender units. The lability of the triterpenoids detected by the method used in this study is also relatively unknown. Killops and Frewin (1994) provide evidence for differential protection of these triterpenols within cutin and wax matrices of mangrove leaves, as well as persistence into the sediments. Volkman et al. (1987) detected many of the same triterpenols in a variety of soils and sediments, also indicating protection or resistance to degradation.

Diagenetic effects on several of the developed parameters were evaluated for a series of degrading *Rhizophora mangle* leaves from a tropical estuary (Hernes et al., 2001). The leaf series consisted of green and senescent leaves from trees, along with yellow, orange (~1 week), brown (~4 weeks), and black (6–7 weeks) leaves either suspended in the water or deposited on the sediment surface. Overall, the green and senescent yellow mangrove leaves from trees exhibit a composition consistent with that expected for fresh angiosperm dicotyledon leaves, with a PD tannin content of <20%, as compared to gymnosperm needles which typically have PD contents >50% (Fig. 4b). Also typical of dicotyledon leaves, the 2,3-*cis* forms in the green and yellow senescent leaves constituted 78% and 73%, respectively, of all extender units, but only 29% and 35% in the terminal units (Fig. 4a). This compares to gymnosperm needles in which 2,3-*cis* forms compose <50% of all extender units (Fig. 4a).

Other source signatures of the green and senescent yellow leaves were (1) degree of polymerization, which at 7.4 and 6.2 are higher by a factor of three than most other dicotyledon leaves (Table 1); (2) flavone content (0.26 and 0.35 wt.%) which is representative of dicotyledons; (3) the presence of triterpenols, which appear to be exclusive to angiosperms and rare in monocotyledons (Gershenzon and Croteau, 1991); and (4) the tannin content of the mangrove leaves (5.2 and 5.4 wt.%) was the highest of the 15 temperate and 25 tropical dicotyledons analyzed (Table 1).

In comparing the black submerged leaves to the senescent yellow leaves from trees, several relevant changes in composition are evident: (1) PD content dropped from 8% to undetected in terminal units and from 19% to 4% overall; (2) flavones were no longer detectable in the black leaves; (3) the 2,3-*cis* content of extender units decreased from 27% to 12% but only from 33% to 29% overall; (4) the calculated degree of polymerization decreased from 6.2 to 3.3; (5) measured total triterpenols increased by a factor of three; and (6) overall tannin content decreased from 5.2 to 0.5 wt.% (Hernes et al., 2001). Thus, while the composition of the black leaves is still recognizable as dicotyledon in origin, it would be difficult to attribute specifically to mangrove leaves if the source was unknown. It is significant to note that in the *Rhizophera mangle* sample set, the triterpenols appeared to be more resistant to degradation than tannin and therefore the combination of compound classes obtained with this analytical method makes it more valuable. Further assessment of diagenetic effects will be necessary to confidently use the parameters and source signals in this study as geochemical source indicators. One intriguing aspect of the mangrove study was that while condensed tannin as measured by this method decreased by 90% between the senescent and black leaves, ^{13}C-NMR indicated that the tannin phenol content in the leaves remained unchanged. Thus, the tannin was being transformed and not remineralized. If the transformation products can be identified using new analytical techniques and related back to the original source compounds, then the parameters developed in this study could be invaluable.

3.10. Comparisons to Lignin and Cutin

Hedges and Mann (1979) and Goñi and Hedges (1992) established source parameters for lignin monomers and dimers, respectively, while Goñi and Hedges (1990) established parameters for cutin. Because lignin and cutin are also unique to terrestrial plants, the yields and compositional parameters they provide are directly comparable to those of tannin (and the identified triterpenoids). Quantitatively, lignin is by far the most abundant of the three biopolymers in woods (cutin is not present in wood), and Hedges and Mann found that angiosperm and gymnosperm woods were readily distinguishable based on syringyl phenol (S) to vanillyl phenol (V) ratios (the former is not obtained from gymnosperms).

Among conifer needles and angiosperm leaves, cutin and tannin are more abundant than lignin. With cutin, gymnosperm/angiosperm distinctions are made primarily by the presence of 14-hydroxytetradecanoic acid, which is only yielded by gymnosperm tissues, although not all. In this study, gymnosperm (conifer) needles are distinguishable on the basis of their low fraction of 2,3-*cis* extender units as well as their high PD tannin content, whereas angiosperm leaves are distinguishable on the basis of flavone and triterpenoid content. Similar to woods, leaf/needle distinctions with lignin are made using S:V vs. cinnamyl (C) to vanillyl (V) phenol ratios.

Among other tissue types, cutin remains the only one of the three biopolymers that can distinguish monocots from dicots. Cutin also appears to be uniquely useful for distinguishing club mosses and ferns. On the other hand, cutin is not present in cones or barks, and neither have been characterized for lignin. Thus, the tannin, triterpenoid, and tetracosanoic acid content measured in this study are the strongest established markers for these often abundant tissue types. Finally, cutin and lignin do not have the overall diversity of compounds that can be found in the flavonoids or triterpenoids, and as such, do not contain unique source markers as, for instance, were found in *Alnus rubra*, *Campsiandra comosa*, or the barks. Thus, the strength of using condensed tannin as a biomarker could lie in its potential to expand as new sources are characterized and new analytical techniques are combined with the one described here.

Table 2. Source identification compounds and parameters.

Source tissue	Species or type	Compound/parameter
Needles	Conifers	PD tannin, 2,3-*cis/trans* ratios, PC:PD:PP percent
Leaves	Dicotyledon	Flavones and triterpenoids
	Alnus rubra	587 triterpenoid
	Campsiandra comosa	PG and PF tannin
	Clarisia racemosa and *Malouetia furfuracea*	Methyl amyrins
Bark	Across types	Tetracosanoic acid
	Conifer	Flavanone
	Alnus rubra and *Zanthoxylum compactom*	Amyrin with 131 mass spectral fragment
Seeds	*Alnus rubra*	Triterpenoid w/ prominent 587 ms fragment
Wood	*Campsiandra comosa*	PG and PF tannin

Abbreviations: PC = procyanidin; PD = prodelphinidin; PP = propelargonidin; PG = proguibourtinidin; PF = profisitinidin.

4. OVERVIEW

A summary of the diagnostic compounds and parameters discussed here is given in Table 2. Clearly, conifers as a whole are the most readily identifiable (as well as quantitatively important) tannin sources. Thus, the analytical method utilized in this study shows promise for studies involving litter and carbon cycling in conifer forests and downstream environments. In addition, flavanones and tetracosanoic acid could provide useful biomarkers in studies related to debarking in the timber industry.

The detection and measurement of triterpenoids in conjunction with tannin provides a powerful complementary tool at two levels of source distinctions. While high triterpenoid yields are indicative of dicotyledons as a whole, triterpenoid compounds unique to individual species (e.g., the "587 compound" from *Alnus rubra*) could show great utility in tracing materials from these specific sources.

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REFERENCES

Appel H. M. (1993) Phenolics in ecological interactions: The importance of oxidation. *J. Chem. Ecol.* **19,** 1521–1551.

Benner R., Hatcher P. G., and Hedges J. I. (1990) Early diagenesis of mangrove leaves in a tropical estuary: Bulk chemical characterization using solid-state ^{13}C NMR and elemental analysis. *Geochim. Cosmochim. Acta* **54,** 2003–2013.

Cowie G. L. and Hedges J. I. (1984) Determination of neutral sugars in plankton, sediments, and wood by capillary gas chromatography of equilibrated isomeric mixtures. *Anal. Chem.* **56,** 497–504.

Eberhardt T. L. and Young R. A. (1994) Conifer seed cone proanthocyanidin polymers: Characterization by 13C NMR spectroscopy and determination of antifungal activities. *J. Agric. Food Chem.* **42,** 1704–1708.

Ellis C. J., Foo L. Y., and Porter L. J. (1983) Enantiomerism: A characteristic of the proanthocyanidin chemistry of the monocotyledonae. *Phytochemistry* **22,** 483–487.

Field J. A. and Lettinga G. (1992) Biodegradation of tannins. In *Metal Ions in Biological Systems. Volume 28: Degradation of Environmental Pollutants by Microorganisms and Their Metalloenzymes.* (eds. H. Sigel and A. Sigel) pp 61–97. Marcel Dekker, Inc., New York.

Gershenzon J. and Croteau R. (1991) Terpenoids. In *Herbivores, Their Interaction With Secondary Plant Metabolites* (eds. G. A. Rosenthal and M. R. Berenbaum), pp. 165–213. Academic Press.

Goñi M. A. and Hedges J. I. (1990) Potential applications of cutin-derived CuO reaction products for discriminating vascular plant sources in natural environments. *Geochim. Cosmochim. Acta* **54,** 3073–3081.

Goñi M. A. and Hedges J. I. (1992) Lignin dimers: Structures, distribution, and potential geochemical applications. *Geochim. Cosmochim. Acta* **56,** 4025–4043.

Harborne J. B., Mabry T. J., and Mabry H., eds. (1975) *The Flavonoids*. Academic Press, New York, 1204 pp.

Harborne J. B., ed. (1988) *The Flavonoids: Advances in Research Since 1980*, Chapman and Hall Ltd., New York, 676 pp.

Harrison P. G. and Durance C. (1989) Seasonal variation in phenolic content of eelgrass shoots. *Aquat. Bot.* **35,** 409–413.

Haslam E. (1989) *Plant Polyphenols—Vegetable Tannins Revisited*. Cambridge University Press, Cambridge, 230 pp.

Hedges J. I. and Mann D. C. (1979) The characterization of plant tissues by their lignin oxidation products. *Geochim. Cosmochim. Acta* **43,** 1803–1807.

Hedges J. I., Clark W. A., Quay P. D., Richey J. E., Devol A. H., Santos U., and De M. (1986) Compositions and fluxes for particulate organic material in the Amazon River. *Limnol. Oceanogr.* **31,** 717–738.

Hedges J. I. and Weliky K. (1989) Diagenesis of conifer needles in a coastal marine environment. *Geochim. Cosmochim. Acta* **53,** 2659–2673.

Hemingway R. W. (1988a) Structural variations in proanthocyanidins and their derivatives. In *Chemistry and Significance of Condensed Tannins* (eds. R. W. Hemingway, J. J. Karchesy), pp. 83–107. Plenum Press.

Hemingway R. W. (1988b) Reactions at the interflavanoid bond of proanthocyanidins. In *Chemistry and Significance of Condensed Tannins* (eds. R. W. Hemingway, J. J. Karchesy), pp. 265–283. Plenum Press.

Hergert H. L. (1989) Hemlock and spruce tannins: An odyssey. In *Chemistry and Significance of Condensed Tannins* (eds. R. W. Hemingway and J. J. Karchesy), pp. 3–20. Plenum Press, New York.

Hernes P. J., Benner R., Cowie G. L., Goñi M. A., Bergamaschi B. A., and Hedges J. I. (2001) Tannin diagenesis in mangrove leaves from a tropical estuary: A novel molecular approach. *Geochim. Cosmochim. Acta* **65,** 3109–3122.

Hernes P. J. and Hedges J. I. (2000) Determination of condensed tannin monomers in plant tissues, soils, and sediments by capillary gas chromatography of acid depolymerization extracts. *Anal. Chem.* **72,** 5115–5124.

Kelsey R. G. and Harmon M. E. (1989) Distribution and variation of extractable total phenols and tannins in the logs of four conifers after 1 year on the ground. *Can. J. Forest Resources* **19,** 1030–1036.

Killops S. D. and Frewin N. L. (1994) Triterpenoid diagenesis and cuticular preservation. *Org. Geochem.* **21,** 1193–1209.

Laks P. E. (1988) Chemistry of the condensed tannin B-ring. In *Chemistry and Significance of Condensed Tannins* (eds. R. W. Hemingway, J. J. Karchesy), pp. 249–263. Plenum Press.

Matthews S., Mila I., Scalbert A., Pollet B., Lapierre C., Herve du Penhoat C. L. M., Rolando C., and Donnelly D. M. X. (1997a) Method for estimation of proanthocyanidins based on their acid depolymerization in the presence of nucleophiles. *J. Agric. Food Chem.* **45,** 1195–1201.

Matthews S., Mila I., Scalbert A., and Donnelly D. M. X. (1997b) Extractible and non-extractible proanthocyanidins in barks. *Phytochemistry* **45,** 405–410.

McGraw G. W. (1988) Reactions at the A-ring of proanthocyanidins. In *Chemistry and Significance of Condensed Tannins* (eds. R. W. Hemingway, J. J. Karchesy), pp. 227–248. Plenum Press.

McMillan C. (1984) The condensed tannins (proanthocyanidins) in seagrasses. *Aquat. Bot.* **20,** 351–357.

Mole S. (1993) The systematic distribution of tannins in the leaves of angiosperms: A tool for ecological studies. *Biochem. Syst. Ecol.* **21,** 833–846.

Patil A. D. and Deshpande V. H. (1982) A new dimeric proanthocyanidin from *Cassia fistula* sapwood. *Indian J. Chem.* **21B,** 626.

Porter L. J. (1989) Condensed tannins. In *Natural Products of Woody Plants I: Chemicals Extraneous to the Lignocellulosic Cell* (ed. J. W. Rowe), pp. 651–690. Springer, Berlin.

Steenkamp J. A., Steynberg J. P., Brandt E. V., Ferreira D. and Roux D. G. (1985) Phlobatannins, a novel class of ring isomerized condensed tannins. *J. Chem. Soc., Chem. Commun.* **23,** 1678–1679.

Thompson R. S., Jacques D., Haslam E., and Tanner R. J. N. (1972) Plant proanthocyanidins. Part 1. Introduction: The isolation, structure, and distribution in nature of plant procyanidins. *J. Chem. Soc. Perkin Trans.* **1,** 1387–1399.

Volkman J. K. (1986) A review of sterol markers for marine and terrigenous organic matter. *Org. Geochem.* **9,** 83–100.

Volkman J. K., Farrington J. W., and Gagosian R. B. (1987) Marine and terrigenous lipids in coastal sediments from the Peru upwelling region at 15°S: Sterols and triterpene alcohols. *Org. Geochem.* **11,** 463–477.

APPENDIX
Molecular data for all samples in weight percent.

		PA Monomers						Phloroglucinol Adducts*								Flavanone, Flavone, Carboxylic A.						Triterpenoids									
Latin Name	TISS.	C	EC	GC	EGC	A	EA	EC	C	EGC	GC	EA	A	PG	PF	T	AP	FS	Q	MR	TCS	bA	aA	MbA	MaA	131A	587	OA	UA	HOA	HUA
Acer macrophyllum	BK	—	0.04	—	—	—	—	0.04	0.01	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Alnus rubra	BK	0.10	0.10	—	—	—	—	0.25	—	—	0.04	—	—	—	—	—	—	—	—	—	0.03	0.23	—	—	—	1.00	—	0.02	—	—	—
Artemisa tridentata	BK	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Quercus garrayana	BK	0.29	0.05	—	—	—	—	0.04	0.04	0.04	0.02	—	—	—	—	—	—	—	0.04	—	—	0.04	0.06	—	—	—	—	—	—	—	—
Thuja plicata	BK	0.38	0.17	—	—	0.05	—	0.13	0.50	—	0.05	0.06	0.13	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Abies holophylla	BK	0.09	0.08	—	—	—	—	0.03	—	—	—	—	—	—	—	—	—	—	—	—	0.26	—	—	—	—	—	—	—	—	—	—
Pinus contorta	BK	0.19	0.02	0.05	—	—	—	0.48	0.06	0.05	0.29	—	—	—	—	0.58	1.25	—	0.02	0.31	0.24	—	—	—	—	—	—	—	—	—	—
Pinus ponderosa	BK	0.58	0.08	—	—	—	—	0.66	0.19	—	0.04	—	—	—	—	0.60	—	—	—	—	0.27	—	—	—	—	—	—	—	—	—	—
Pseudotsuga menziesii	BK	0.15	0.19	—	—	—	—	0.32	0.18	—	—	—	—	—	—	2.28	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Tsuga heterophylla	BK	2.18	2.24	0.01	0.02	1.07	1.94	2.11	0.77	—	0.23	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Aniba guianensis	BK	0.13	0.10	—	—	—	—	0.20	0.05	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Clarisia racemosa	BK	—	0.01	—	—	0.00	0.01	0.00	0.01	—	—	0.02	0.00	—	—	—	—	—	—	—	—	0.03	0.16	—	0.07	—	—	—	—	0.63	—
Crescentia amazonica	BK	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Genipa americana	BK	—	0.00	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.01	—	—	—	—	—	—	—	—	—
Nectandra amazonium	BK	0.23	0.29	—	—	—	—	0.67	0.10	—	0.03	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Neoxythece elegans	BK	—	0.00	0.04	0.01	—	—	0.06	0.03	0.15	0.35	—	—	—	—	—	—	—	—	—	—	1.10	1.10	—	—	—	—	0.84	—	0.16	—
Xylosma intermedium	BK	0.03	—	—	—	—	—	0.01	0.00	—	0.01	—	—	—	—	—	—	—	—	—	—	0.01	0.01	—	—	—	—	0.01	—	—	—
Zanthoxylum compactum	BK	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.02	—	—	—	1.98	—	—	—	—	—
Larix occidentalis	C	0.12	0.04	—	—	—	—	0.60	0.08	—	0.03	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Picea sitchensis	C	0.14	0.01	0.01	—	—	—	0.05	0.02	0.03	0.03	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Pinus ponderosa	C	0.26	0.02	—	—	—	—	0.24	0.14	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Pseudotsuga menziesii	C	0.18	0.22	—	—	—	—	1.44	0.16	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Tsuga heterophylla	C	0.26	0.07	0.06	0.02	—	0.01	0.68	0.18	0.38	1.46	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Sequoia sempervirens	C	0.20	0.09	0.03	0.02	—	—	0.15	0.13	0.39	0.78	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Alnus rubra	S	0.07	0.29	—	—	—	—	1.41	0.10	—	—	—	—	—	—	—	—	—	—	—	—	0.17	0.04	—	—	0.20	4.13	—	—	—	—
Acer macrophyllum	GL	0.19	0.07	0.02	—	—	—	0.22	0.01	0.04	0.08	—	—	—	—	—	—	—	0.22	—	—	0.05	0.19	—	—	—	—	—	—	—	—
Alnus rubra	GL	0.15	0.17	—	—	—	—	0.56	0.03	—	0.05	—	—	—	—	—	—	—	0.93	—	—	0.10	—	—	—	—	0.25	—	—	—	—
Artemisa tridentata	GL	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Avicennia germinans	GL	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Camellia spp.	GL	0.50	2.04	—	—	—	—	0.62	0.56	—	—	—	—	—	—	—	—	—	0.58	—	—	0.01	0.02	—	—	—	—	—	—	—	—
Ilex aquifolium	GL	—	0.02	—	—	—	—	0.01	—	—	—	—	—	—	—	—	—	—	—	—	—	0.08	0.62	—	—	—	—	0.51	2.19	—	—
Malus spp.	GL	0.02	0.10	—	—	—	—	0.39	—	—	—	0.37	—	—	—	—	—	—	1.57	—	—	—	—	—	—	—	—	0.15	0.77	0.05	0.13
Populus trichocarpa	GL	0.33	0.01	0.05	—	—	—	1.13	0.18	—	0.43	—	—	—	—	—	—	—	0.09	—	—	—	—	—	—	—	—	—	—	—	—
Quercus garrayana	GL	0.72	0.52	0.03	—	—	—	0.46	0.17	0.16	0.16	—	—	—	—	—	—	—	0.42	—	—	—	—	—	—	—	—	0.15	0.05	—	—
Quercus palustris	GL	0.36	—	—	—	—	—	0.20	0.04	—	—	—	—	—	—	—	—	—	0.02	0.33	—	0.21	0.28	—	—	—	—	0.14	0.11	—	—
Quercus robur	GL	0.25	—	—	—	—	—	0.15	0.02	—	0.03	—	—	—	—	—	—	—	—	—	—	0.03	0.07	—	—	—	—	—	—	—	—
Quercus rubra	GL	—	0.37	—	—	—	—	0.25	0.02	—	—	—	—	—	—	—	—	—	—	—	—	0.21	0.19	—	—	—	—	—	—	—	—
Rosa spp.	GL	0.75	0.08	0.03	—	—	—	0.71	0.14	—	—	—	—	—	—	—	—	—	0.23	—	—	—	—	—	—	—	—	0.04	0.03	0.02	0.02
Rubus spp.	GL	—	0.07	—	—	—	—	0.02	—	—	—	—	—	—	—	—	—	0.23	0.73	—	—	—	—	—	—	—	—	—	—	—	—
Vitis spp.	GL	0.33	0.43	0.16	0.17	—	—	1.42	0.11	0.45	1.60	—	—	—	—	—	—	0.17	1.72	—	—	—	—	—	—	—	—	—	—	—	—
Aniba guianensis	GL	0.12	0.11	—	—	—	—	0.35	0.02	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Aspidosperma rigida	GL	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Bothriospora lorymbosa	GL	—	—	—	—	—	—	0.17	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.05	0.03	—	—
Buchenavia oxycarpa	GL	—	—	—	—	—	—	0.01	—	—	0.01	—	—	—	—	—	—	—	—	—	—	—	0.03	—	—	—	—	0.04	0.01	0.02	—
Campsiandra comosa	GL	0.53	0.23	—	—	0.07	0.02	0.17	—	—	0.05	—	—	0.19	0.07	—	—	—	0.23	0.30	—	—	—	—	—	—	—	—	—	—	—
Caraipa grandifolia	GL	0.04	0.19	—	—	—	—	0.41	—	—	0.06	—	—	—	—	—	—	—	—	—	—	—	0.13	—	—	—	—	—	0.02	0.03	—
Clarisia racemosa	GL	0.13	0.08	—	—	0.08	0.13	0.37	—	—	—	0.68	0.12	—	—	—	—	—	—	—	—	0.02	0.03	0.04	0.11	—	—	—	—	—	—
Genipa americana	GL	0.02	0.04	—	—	—	—	0.03	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.14	1.41	—	—
Glycydendron amazonicum	GL	0.08	—	0.03	—	—	—	0.34	0.09	0.18	0.46	0.02	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Guarea rubiflora	GL	0.06	0.17	0.00	0.00	—	—	0.46	0.02	0.13	0.44	—	—	—	—	—	—	—	—	—	—	0.02	0.04	—	—	—	—	—	—	—	—
Guarea trichilioides	GL	0.24	0.22	—	—	—	—	0.86	0.20	—	0.01	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Lecointea amazonica	GL	—	—	—	—	—	—	0.03	—	—	0.00	—	—	—	—	—	—	—	—	—	—	0.05	0.09	—	—	—	—	—	—	—	—
Leonia racemosa	GL	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Malouetia furfuracea	GL	0.20	0.28	0.06	0.03	0.04	0.06	0.30	0.09	—	—	0.76	0.27	—	—	—	—	—	—	—	—	0.12	0.65	0.05	0.31	—	—	0.26	1.35	—	—
Nectandra amazonium	GL	0.11	0.12	—	—	—	—	0.40	0.01	—	—	—	—	—	—	—	—	—	0.21	—	—	—	—	—	—	—	—	—	—	—	—
Neoxythece elegans	GL	—	0.06	0.14	0.12	—	—	0.14	—	—	0.68	—	—	—	—	—	—	—	0.04	0.43	—	0.13	0.06	—	—	—	—	—	—	—	—
Pterocarpus amazonicus	GL	—	0.05	0.02	0.02	—	—	0.11	—	0.05	0.28	—	—	—	—	—	—	—	—	—	—	—	0.06	—	—	—	—	—	—	—	—
Rhizophora mangle	GL	0.49	0.18	0.02	0.02	—	—	3.56	0.31	0.01	0.63	—	—	—	—	—	—	—	0.26	0.06	—	0.04	0.02	—	—	—	—	—	—	—	—
Symmeria paniculata	GL	0.05	0.56	—	—	—	—	0.91	0.03	—	—	0.02	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Tabebuia barbata	GL	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.42	1.14	0.11	0.18
Vatairea guianensis	GL	0.09	0.02	—	—	0.13	—	0.02	—	—	—	0.10	—	—	—	—	—	—	—	—	—	0.03	0.13	—	—	—	—	—	—	—	—

Vitex cymosa	GL	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.03	0.06	0.27	0.54
Xylopia callophylla	GL	0.07	0.32	—	—	—	—	0.97	0.02	—	—	—	—	—	—	—	—	—	0.18	—	—	—	—	—	—	—	—	—	—	—	
Xylosma intermedium	GL	0.14	0.02	—	—	—	—	0.10	0.02	—	—	—	—	—	—	—	—	—	—	—	—	0.01	0.04	—	—	—	—	—	—	—	
Zanthoxylum compactum	GL	0.11	0.24	—	—	—	—	0.64	0.01	—	—	—	—	—	—	—	—	—	0.31	—	—	—	—	—	—	—	—	—	—	—	
Araucaria araucana	GL	0.31	0.07	0.03	0.03	0.02	0.03	0.66	0.07	0.23	0.97	0.07	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Thuja plicata	GN	1.18	0.32	—	—	0.05	0.02	0.40	0.26	1.50	1.27	0.06	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Abies marocana	BN	1.20	0.21	0.68	0.11	0.01	—	0.78	0.33	0.75	1.89	0.06	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Abies nebrodensis	BN	1.12	0.12	0.92	0.04	—	—	0.66	0.21	0.79	2.35	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Picea engelmannii	GN	0.51	0.11	0.05	—	—	—	1.24	0.08	—	0.37	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Picea sitchensis	BN	0.36	0.09	—	—	0.00	—	0.86	0.03	—	0.02	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Pinus contorta	GN	1.04	0.14	0.99	0.02	—	—	1.01	0.40	1.67	4.64	0.07	—	—	—	0.08	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Pinus ponderosa	GN	0.83	0.09	0.57	0.03	—	—	1.24	0.16	0.59	5.08	0.05	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Pseudotsuga menziesii	GN	0.33	0.22	0.08	0.08	—	—	1.81	0.14	0.35	2.52	0.04	—	—	—	0.03	—	0.66	0.84	—	—	—	—	—	—	—	—	—	—	—	
Tsuga heterophylla	GN	0.24	0.10	—	0.02	—	—	0.86	0.05	0.40	2.96	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Sequoia sempervirens	GN	0.44	0.06	0.19	0.09	—	—	0.70	0.26	0.86	2.88	—	0.01	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Sequoiadendron giganteum	GN	0.28	0.06	0.06	0.03	—	—	0.79	0.07	0.24	1.24	—	—	—	—	—	—	—	0.28	—	—	—	—	—	—	—	—	—	—	—	
Taxodium distichum	GN	0.44	0.09	0.08	—	—	—	1.18	0.11	0.45	1.89	—	—	—	—	—	—	—	0.54	—	—	—	—	—	—	—	—	—	—	—	
Taxodium distichum	GN	0.27	0.05	0.05	—	—	—	0.88	0.06	0.21	1.25	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Alnus rubra	W	0.23	0.02	0.02	—	—	—	0.27	0.05	—	0.03	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Thuja plicata	W	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Picea sitchensis	W	—	—	—	—	—	—	0.01	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Picea spp.	W	—	—	—	—	—	—	0.01	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Pseudotsuga menziesii	W	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.01	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Bothriospora lorymbosa	W	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.14	—	—	
Buchenavia oxycarpa	W	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Campsiandra comosa	W	0.21	0.02	—	—	—	—	0.05	0.02	—	—	—	—	0.01	0.10	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Clarisia racemosa	W	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Leonia racemosa	W	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Neoxythece elegans	W	—	0.00	—	—	—	—	0.00	—	—	0.00	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Symmeria paniculata	W	0.15	0.18	—	—	—	—	0.25	0.02	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Tabebuia barbata	W	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Vitex cymosa	W	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Xylopia callophylla	W	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Xylosma intermedium	W	—	0.01	—	—	—	—	0.02	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Rhacomitrium aciculare	WP	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Rhytidiadelphus loreus	WP	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Lycopodium sitchense	WP	—	—	—	—	—	—	0.02	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Polystichum acrostichoides	WP	0.04	0.10	—	0.02	—	—	0.80	—	—	0.06	0.07	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Pteridium aquilinium	WP	—	0.07	—	0.03	—	0.02	0.51	—	0.03	0.22	0.05	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Equisetum telmateia	WP	—	—	—	—	0.00	0.03	0.72	—	—	—	0.49	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Alaria fistulosa	B	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Alaria fistulosa	ST	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Laminaria longpipes	WP	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Thalasiophylum	WP	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Agrostis alba	WP	—	—	—	—	—	—	0.00	—	—	0.01	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Avena spp.	WP	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Carex spp.	WP	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Salicornia spp.	WP	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.12	—	—	
Spartina alterniflora	WP	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.02	0.08	—	—	—	—	—	—	—	
Zostera spp.	WP	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Echinochloa polystachya	WP	—	—	—	—	—	—	0.00	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Eichornia crassipes	WP	—	0.04	—	—	—	0.03	0.24	—	—	—	0.11	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Gynerium sagittatum	WP	0.00	—	—	—	—	—	—	0.01	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Paspalum repens	WP	—	0.02	—	—	—	—	0.02	—	—	—	—	—	—	—	—	—	—	0.34	—	—	—	—	—	—	—	—	—	—	—	
Pistia stratoides	WP	—	—	—	—	—	—	0.01	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Salvinia auriculata	WP	—	0.08	—	—	—	0.05	1.23	0.02	—	—	0.08	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	

* 4α and 4β adducts for each compound have been summed.

Abbreviations: Compounds: C = catechin, EC = epicatechin, GC = gallocatechin, EGC = epigallocatechin, A = afzelechin, EA = epiafzelechin, PG = proguibourtinidin, PF = profisitinidin, T = taxifolin (dihydroquercetin), AP = ampelopsin (dihydromyricetin), FS = fisetin, Q = quercetin, MR = myricetin, TCS = tetracosanoic acid, bA = β-amyrin, aA = α-amyrin, MbA = methyl-β-amyrin, MaA = methyl-α-amyrin, 131A = amyrin with 131 mass spectral fragment, 587 = triterpenoid with prominent 587 mass spectral fragment, OA = oleanolic acid, UA = ursolic acid, HOA = hydroxyoleanolic acid, HUA = hydroxyursolic acid.

Tissue types: BK = bark, C = cone, S = seedpod, GL = green leaves, GN = green needles, BN = brown needles, WP = whole plant, W = wood, B = blade, ST = stipe.