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Lignin Pyrolysis Products, Lignans, and Resin Acids as Specific Tracers of Plant Classes in Emissions from Biomass Combustion

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Biomass smoke aerosols contain thermally unaltered and partially altered biomarker compounds from major vegetation taxa. These compounds range from C_8 to C_{31} and include phytosterols, lignans, phenolic products from lignin, and diterpenoids from resins. Certain of the higher molecular weight biomarkers are vaporized from the parent plant material and subsequently condense unaltered into the particle phase. Other compounds undergo pyrolytic alteration and possibly dimerization. In both cases it is possible to assign many of these compounds to the plant taxa of the unburned fuel. The diterpenoids are good indicators for smoke from burning of gymnosperm wood. The relative distribution of the OH/OCH_3 substituent patterns on the phenolic products indicates the plant class of the biomass that was burned. Application of these relationships to the interpretation of ambient smoke aerosols may permit further evaluation of the sources that contribute to regional biomass burning.

Introduction

Emissions from biomass combustion have received considerable attention in recent years (*1–4*). On a global basis, the particulate emissions from combined anthropogenic and natural background biomass burning may influence atmospheric chemical, optical, and radiative properties through direct (absorption and scattering of solar and terrestrial radiation) and indirect (modification of cloud processes) mechanisms (*5, 6*). It is difficult to assess the magnitude of biomass burning because it is not a regulated activity and is practiced globally for such diverse purposes as clearing forests, home heating, weed and pest control, waste disposal, and food preparation (*1, 7*). Estimates of the particulate emissions from biomass burning are currently $\sim 1 \times 10^{11}$ kg of carbon/year (*4*). In order to refine such mass emission estimates and to assess the relative importance of emissions from various biomass burning activities to the tropospheric boundary layer, specific and characteristic tracers for "biofuel" combustion would be very useful.

Previous assessments of biomass emissions using combustion byproducts as tracers have studied the following: (1) combustion gases such as NO_x, HCN, CH_3CN, CH_4, saturated C_2–C_5 hydrocarbons, CO, and CO_2 (e.g., refs 7–12); (2) macromolecular smoke particles in the form of charcoal or soot (e.g., refs 13–16); and (3) solvent-soluble organic compounds isolated from smoke particulate matter such as polynuclear aromatic hydrocarbons (PAH) (e.g., refs 17–20) or phenols (*21–24*). Macromolecular smoke particles are difficult to characterize, and gaseous emissions are not necessarily specific tracers for biomass combustion since they are also emitted from other processes. PAH have multiple sources, although retene does correlate with a specific origin from conifer wood or coal combustion (*18, 25, 26*). Specific phenolic compounds have been identified in wood smoke (*22–24*) and have been interpreted as pyrolysis products released during hardwood or softwood burning (cf. refs 20 and 27). Likewise, the combustion of resinous wood from coniferous trees (e.g., pine and spruce) releases unaltered and partially altered diterpenoids which are useful markers in tracing coniferous wood combustion in the atmosphere (*25*). Thus, these earlier tracer studies show the intermediate molecular weight fractions of smoke aerosols (C_{10}–C_{40} range) contain potentially useful organic compounds that retain their source-specific chemical nature.

In other aerosol source characterization work that focused on the same solvent-soluble range of organic matter, we have noted that thermally labile compounds, such as cholesterol and oleic acid, in beef are emitted directly without molecular alteration into smoke during grilling and frying (*28*). Thus, cholesterol has been proposed as one of the molecular tracers for assessing emissions from cooking. Here we characterize other thermally unaltered and partially altered organic tracers in smoke from major plant classes (taxa). The phenolic breakdown products from lignin precursors and the unaltered or partially altered compounds such as lignans, phytosterols, and resin constituents are discussed here as biomarker tracers. Our study uses samples obtained from direct source sampling of smoke emissions from hard- (oak, *Quercus agrifolia*) and softwoods (pine, various *Pinus*) combustion experiments (*29*) and combines this information with chemotaxonomic studies of known natural emissions of higher molecular weight organic substances from burned and unburned vegetation, including samples from grassland burning (seed grass; e.g., *Lolium perenne*) previously reported by Standley (*30*). It is important to be able to differentiate between biomass burning of various vegetation taxa. Therefore, specific and characteristic tracers will be sought which allow the distinction of emissions from biomass burning of grass and coniferous and deciduous trees and which provide the means to trace such emissions in the atmosphere.

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Experimental Methods

Source Sampling Program. A dilution stack sampler was designed and field-evaluated for the collection of fine organic aerosols ($d_p \leq 2$ μm) from several combustion sources (*31*). The sampler simulates the cooling and dilution processes that occur in the plume downwind of a combustion source, so that the organic compounds which condense onto preexisting particles under ambient conditions are collected in the sampler as particulate matter. To ensure collection of a representative aerosol sample, the following design goals were established for the sampler (*31*): (1) dimensions of the sampler chosen to minimize the loss of particles and the condensation of supersaturated vapors onto wall surfaces, (2) atmospheric dispersion processes simulated by ensuring that the emissions were diluted and cooled to ambient temperature before sample collection, and (3) sufficient residence time provided in the sampler to allow complete condensation of the supersaturated vapors.

Fine aerosol samples were collected from the residence time chamber at the downstream end of the sampling system. Aerosol samples for organic analysis were withdrawn through several parallel AIHL cyclone separators (27.9 ± 0.3 L/min) each, which removed particles with aerodynamic diameters greater than or equal to 2.0 μm. Downstream of this bank of cyclone separators, a set of typically 15 quartz fiber filters (Pallflex 2500 QAO; 47-mm diameter) arranged in parallel was used as the collection substrate, with a flow rate of 9.0–9.6 L/min through each filter. The quartz filters were preheated prior to use at 750 °C for at least 2 h to reduce the carbon blank associated with new filters.

Wood combustion experiments were conducted using a traditional brick fireplace in an older single-family home. Separate burns were conducted using pine as a softwood and oak as a hardwood. For each experiment, a few pieces of newspaper were used to start the fire, but otherwise the material being burned (including the kindling) was strictly limited to the particular wood being utilized. Samples were collected over the entire course of each fire (~3 h), from ignition until only glowing embers remained. Further details of sampler design and sample acquisition procedures adopted for the wood smoke source tests are presented elsewhere (*29, 31, 32*).

Sample Extraction. Micromethods have been developed for the quantitative recovery of extractable organic matter in the atmospheric fine aerosol fraction (*32–35*). The analytical protocol is designed to monitor losses associated with volatilization, incomplete extraction, or instrumental bias. To provide sufficient organic mass for the instrumental analyses (i.e., minimum of 300 μg of organic carbon/filter composite), up to 18 separate parallel filters were combined for extraction. The organic matter was extracted from the filters by mild ultrasonic agitation using successive additions of *n*-hexane (two volume additions) and benzene/2-propanol (2:1; three volume additions). The extracts were filtered, combined, and then reduced to volumes of ~2 mL. The neutral fraction is defined operationally as that fraction which elutes from the bonded phase (DB-1701) of the gas chromatographic column and is detected by the flame ionization detector (FID) or mass spectrometer without further derivatization. An aliquot of the total extract was derivatized by addition of diazomethane (*33*), which converted reactive organic OH functionalities to the respective methyl ester or methyl ether analogs. Analysis of this derivatized fraction by gas chromatography (GC) and GC/mass spectrometry (MS) produced data for the acid plus neutral fraction.

Instrumental Analysis. Extracts from the fine carbon particle samples were analyzed using a Varian 4600 high-resolution gas chromatograph (HRGC) fitted with a Grob injector (splitless mode and temperature at 300 °C). A-30 m fused-silica DB-1701 column was used (bonded 86% dimethyl 14% (cyanopropyl)phenylpolysiloxane, 25-μm film thickness, 0.32-mm i.d.; J&W Scientific, Rancho Cordova, CA). The HRGC was equipped with a FID and was operated at the maximum range of sensitivity (10^{-12} mV/A at an attenuation of 1). Temperature programming consisted of injection at 65 °C, isothermal hold at 65 °C for 10 min, temperature ramp of 10 °C/min for 21 min, followed by isothermal hold at 275 °C for 49 min. Mass spectrometric analyses were conducted using a Finnigan Model 4000 quadrupole mass spectrometer interfaced with a gas chromatograph and an Incos data acquisition system. The organic compounds were ionized by electron impact with an electron energy of 70 eV. The scanning frequency was set to 0.5 s^{-1}, ranging from 50 to 550 Da. The GC column, temperature programming, and time settings used were identical to the HRGC operating conditions. Further details of the analytical protocol and the quality assurance procedures can be found in Mazurek et al. (*32–35*) and Rogge et al. (*28, 36*).

Compound Identification

Compound identifications are based on comparisons with authentic standards, GC retention times, literature mass spectra (e.g., ref 22) and interpretation of mass spectrometric fragmentation patterns. The mass spectra and interpretations of the fragmentation patterns of various lignans have been published as the underivatized and methylated species (*37–40*). In general, these compounds exhibit strong molecular ions and often base peak fragments due to benzylic cleavage. Some mass spectra of silylated lignan derivatives have also been published (*41*). They show strong molecular ions, with minor loss of CH_3 from M^+, and base peak fragments due to benzylic cleavage (*41*). The mass spectra of the lignans are characteristic, and therefore these compounds can be positively identified on the basis of the interpretation of the fragmentation pattern combined with the GC retention index. The yields of the marker compounds are reported as emission rates in milligram per kilogram of biomass burned (*42*).

Results and Discussion

The total extracts of the fine particles contained in wood smoke emissions comprise resolved compounds (potential molecular tracers) and an unresolved complex mixture (UCM) of compounds in the GC or GC/MS analyses. Two such examples of GC traces, as the methylated derivatives, are shown in Figure 1. Pyrolysis (thermal alteration) products have been characterized in smoke from biomass combustion (*18, 22, 23*). However, direct volatilization of higher molecular weight organic compounds into smoke has not been documented as an injection mechanism for tracers to the atmosphere. It is a process analogous to steam distillation/stripping and has been described for meat frying and grilling (*28*) and for roofing tar pot

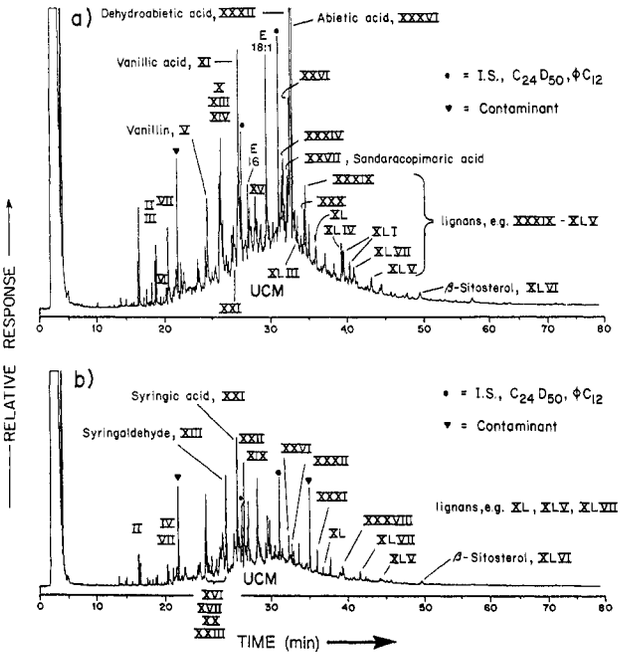

Figure 1. Gas chromatograms of total extracts (methylated with diazomethane) from fine particles of (a) pine wood smoke and (b) oak wood smoke. Roman numerals refer to compounds in Table I and their structures are shown in Figure 2: E16, *n*-hexadecanoic acid; E18:1, *n*-octadecenoic acids; UCM, unresolved complex mixture of compounds, typically branched and cyclic hydrocarbons.

emissions (*43, 44*). Thus, volatilization is expected to be an excellent mechanism for the introduction of oxygenated organic compounds, especially those with low vapor pressures, into smoke and ultimately into the atmosphere. Condensation of such high molecular weight organic compounds onto preexisting fine particulate matter when the smoke plume is diluted and cooled in the atmosphere provides the means for incorporation of such marker compounds into the aerosol phase.

(i) Resin Acids. Resin acids such as abietic or pimaric acids are biosynthesized mainly by conifers (gymnosperms) in temperate regions. Deciduous trees in tropical zones are prolific resin and mucilage (gum) producers, but compositional data on smoke from such sources show no resin acids (e.g., ref 45). Derivatives of these resin compounds at various stages of diagenetic or thermal alteration have been found in ambient aerosols (*35, 46–51*) and in smoke particles from slash burning (*25, 30, 52*). The unaltered compounds are also present at significant concentrations. This is shown in the GC traces of Figure 1 and in Table I, where the major compounds in the total lipid material from the pine wood smoke are diterpenoid acids, namely, dehydroabietic (**XXXII**), abietic (**XXXVI**), sandaracopimaric (**XXXIV**), and pimaric (**XXXIII**) acids, with minor amounts of isopimaric acid (**XXXV**), 7-oxo-dehydroabietic acid (**XXXVII**), and retene (**XXIV**) (note—all the chemical structures are given in Figure 2 and the Roman numerals refer to the compounds listed in Table I according to increasing molecular weight). The diterpenoid acids are also indicated in the mass fragmentograms of the GC/MS data for the extracts from pine smoke (Figure 3). The dominant compound in pine smoke is dehydroabietic acid [the quantitative data for all compounds emitted is the topic of a separate publication by Rogge et al. (*42*)]. A minor amount of dehydroabietic acid and traces of some of the other resin acids are detectable in the oak smoke (Figure 1b). This is probably due to the prior combustion of pine wood in the same fireplace and revaporization of deposited compounds by the oak fire, which burned at higher temperatures (*43*). Smoke from alder combustion did not contain compounds derived from resin acids (*52*). Dehydroabietic and 7-oxo-dehydroabietic acids can be regarded as partially altered products from conifer resin acids, and the other diterpenoid acids are directly volatilized unaltered compounds. Retene is a higher temperature alteration product of resin diterpenoids and is present in the pine wood smoke at trace levels (results not shown, cf. Table I), but is not detectable in the oak wood smoke.

Several of these diterpenoid acids and retene were found in extracts of fine ambient aerosol samples collected from the Los Angeles air basin during an intensive sampling program that was conducted over an entire calendar year, 1982 (*36*). The annual concentration pattern of these resin constituents followed the heating season, with highest concentrations observed for winter months and only minor ambient concentrations during summer. This resin marker concentration pattern present in the ambient aerosol samples was consistent with estimates of wood smoke emissions given for the Los Angeles area over an entire annual cycle (*53*).

(ii) Phytosterols. Sterols, as produced by marine and terrestrial biota, range from C_{25} to C_{30}, generally with C_{27} and C_{29}, respectively, predominating (*54, 55*). Phytosterols (sterols of higher plants) comprise C_{28} and C_{29} sterols, with β-sitosterol (C_{29}, **XLVI**) as the major consitutent (e.g., refs 56–58). Algal (e.g., phytoplankton, diatoms) detritus contains sterol distributions different from those of vascular plants, often with a predominance of cholesterol (C_{27}) (*57, 59*), and faunal sterols consist primarily of cholesterol (*58*).

Sterols measured in aerosols over rural and urban areas in the temperate western United States were found to have a predominance of cholesterol, whereas sterols in aerosols of semiarid Nigeria and southeastern Australia were dominated by β-sitosterol (*55, 60*). Further sterol distributions have been reported for aerosols in various global regions, both continental and oceanic (*26, 45, 56, 61-66*).

The shift in sterol carbon number maximum may be useful in identifying particulate matter from different source areas. Thus, the occurrence of β-sitosterol (C_{29}) in aerosols indicates the presence of plant-derived material. Cholesterol (C_{27}) in aerosols could be contributed by plant microbiota in remote areas and from meat cooking operations and other faunal sources in urban areas.

The major phytosterol found in smoke from the present pine and oak wood combustion experiments is β-sitosterol (**XLVI**, Figure 1), the thermally unaltered compound. Similar results have also been found for smoke from alder wood and grass (ref 56 and Simoneit, Standley, and Chen, unpublished data). The thermal dehydration or pyrolysis products of phytosterols, such as sterones, steradienes, etc. (e.g., ref 67), are not detectable in any of the smoke samples from wood or grass examined here.

(iii) Lignin Pyrolysis Products. Lignin, an essential and major biopolymer of woody tissue, is derived primarily from three aromatic alcohols, *p*-coumaryl, coniferyl, and sinapyl alcohols (Figure 4) (*68*), and the degradation products from oxidation or pyrolysis are classified as coumaryl, vanillyl, and syringyl moieties, respectively (*69*).

Table I. Major Compounds Proposed as Tracers for Lignin Pyrolysis Products, Lignans, and Resin Acids in Smoke from Biomass Combustion

structure no.[a]	compound	compd[b]	MS (key ions and M+)[b,c]	compd ID[d]	source concn[e]		
					pine	oak	grass
I	anisaldehyde	$C_8H_8O_2$	136	S	0.7	nd	++
II	4-methyl-2-methoxyphenol	$C_8H_{10}O_2$	138	F	35	13	nd
III	1-(4-methoxyphenyl)propane	$C_{10}H_{14}O$	150	F	nd	nd	+
IV	1-methyl-3,4-dimethoxybenzene	$C_9H_{12}O_2$	152	F	28	nd	nd
V	vanillin	$C_8H_8O_3$	152	S	29	2	nd
VI	anisic acid	$C_9H_{10}O_3$	166	S	4	8	+++
VII	1-guaiacylpropane	$C_{10}H_{14}O_2$	166	I	20	3	nd
VIII	veratraldehyde	$C_9H_{10}O_3$	151, *166*	S	23	5	nd
IX	homoanisic acid	$C_{10}H_{12}O_3$	180	F	nd	nd	+
X	guaiacylacetone	$C_{10}H_{12}O_3$	180	F	39	11	nd
XI	vanillic acid	$C_9H_{10}O_4$	182	S	65	19	nd
XII	1-(3,4-dihydroxy-5-methoxyphenyl)ethanone	$C_9H_{10}O_4$	*167*, 182	F	nd	21	nd
XIII	syringaldehyde	$C_9H_{10}O_4$	182	S	nd	67	nd
XIV	3,4-dimethoxyphenylacetone	$C_{11}H_{14}O_3$	194	F	10	6	nd
XV	homovanillic acid	$C_{10}H_{12}O_4$	196	S	83	15	nd
XVI	veratric acid	$C_{10}H_{12}O_4$	196	S	65	19	nd
XVII	1-(3,5-dimethoxy-4-hydroxyphenyl)ethanone	$C_{10}H_{12}O_4$	196	F	nd	56	nd
XVIII	homoveratric acid	$C_{11}H_{14}O_4$	210	F	6	nd	nd
XIX	1-syringylethanone	$C_{11}H_{14}O_4$	210	F	nd	21	nd
XX	1-(3,4,5-trimethoxyphenyl)ethanone	$C_{11}H_{14}O_4$	210	I	nd	36	nd
XXI	syringic acid	$C_{10}H_{12}O_5$	212	F	nd	23	nd
XXII	1-(3,4,5-trimethoxyphenyl)propanone	$C_{12}H_{16}O_4$	224	F	nd	80	nd
XXIII	3,4,5-trimethoxybenzoic acid	$C_{11}H_{14}O_5$	226	S	nd	23	nd
XXIV	retene	$C_{18}H_{18}$	*219*, 234	S	0.7	0.1	nd
XXV	dianisyl	$C_{16}H_{18}O_2$	*227*, 242	I	nd	nd	+
XXVI	divanillyl	$C_{16}H_{18}O_4$	*137*, 274	I	22	2	nd
XXVII	bis(3,4-dimethoxyphenyl)methane	$C_{17}H_{20}O_4$	*151*, 288	I	6	0.8	nd
XXVIII	divanillylmethane	$C_{17}H_{20}O_4$	*137*, 152, 288	I	6	0.8	nd
XXIX	diveratryl	$C_{18}H_{22}O_4$	*151*, 302	I	18	0.5	nd
XXX	1,2-divanillylethane	$C_{18}H_{22}O_4$	*137*, 165, 320	I	1	nd	nd
XXXI	bis(guaiacylsyringyl)	$C_{16}H_{18}O_5$	137, *167*, 304	I	nd	3	nd
XXXII	dehydroabietic acid	$C_{21}H_{30}O_2$	*239*, 314	S	37	6	nd
XXXIII	pimaric acid	$C_{21}H_{32}O_2$	*121*, 316	S	24	nd	nd
XXXIV	sandaracopimaric acid	$C_{21}H_{32}O_2$	*121*, 316	S	47	nd	nd
XXXV	isopimaric acid	$C_{21}H_{32}O_2$	*105*, 241, 316	S	7	nd	nd
XXXVI	abietic acid	$C_{21}H_{32}O_2$	316	S	1	nd	nd
XXXVII	7-oxodehydroabietic acid	$C_{21}H_{28}O_3$	*253*, 328	S	3	nd	nd
XXXVIII	disyringyl	$C_{18}H_{22}O_6$	*167*, 334	I	nd	7	nd
XXXIX	tetrahydro-3,4-divanillylfuran	$C_{20}H_{24}O_5$	*137*, 344	I	23	0.6	nd
XL	tetrahydro-3-vanillyl-4-veratrylfuran	$C_{21}H_{26}O_5$	137, *151*, 358	I	9	0.4	nd
XLI	matairesinol	$C_{20}H_{22}O_6$	*137*, 358	L (*37*)	3	nd	nd
XLII	bis(3,4,5-trimethoxyphenyl)ethane	$C_{20}H_{26}O_6$	*181*, 362	I	nd	0.8	nd
XLIII	tetrahydro-3,4-diveratrylfuran	$C_{22}H_{28}O_5$	*151*, 372	I	4	0.1	nd
XLIV	dihydro-3,4-diveratryl-2(3*H*)-furanone	$C_{22}H_{26}O_6$	*151*, 386	I	2	nd	nd
XLV	dihydrovanillylsyringyl-2(3*H*)-furanone and isomers	$C_{22}H_{26}O_7$	137, 151, 167, *181*, 402	I	5	nd	nd
XLVI	β-sitosterol	$C_{29}H_{50}O$	*55*, 213, 414	S	46	10	+
XLVII	dihydro-3-(2′,3′,4′-trimethoxyphenyl)-4-veratryl-2(3*H*)-furanone and isomers	$C_{23}H_{28}O_7$	151, *181*, 416	I	5	nd	nd

[a] See Figure 2. [b] Given as the methyl esters for the carboxylic acids and both as free phenols (found in the neutral fraction prior to derivatization) and as permethyl ethers (found in the methylated fraction) for oxy aromatics. [c] Base peak of the mass spectrum is italicized. [d] Basis for identification: S, comparison with authentic standard; L, comparison with literature mass spectrum; F, comparison with MS in library file; I, interpretation of fragmentation pattern and retention time of analogous compound. [e] Source concentration is given as emission rate in milligrams per kilogram of biomass burned (*42*). Pine representative for gymnosperms, oak representative for angiosperms; for grass only relative concentration data taken. nd, not detected; +, present.

The *proportions* of these biomonomers vary considerably among the major plant classes. Thus, lignins of hardwoods (angiosperms) are enriched in products from sinapyl alcohol, softwoods (gymnosperms) instead have a high proportion of products from coniferyl alcohol with a minor component from sinapyl alcohol, and grasses have mainly products from *p*-coumaryl alcohol (*70*).

Pyrolyses of lignin and wood yield the breakdown products of the biopolymers as phenols, aldehydes, ketones, acids, and alcohols, generally with the retention of the original substituents (OH, OCH_3) on the phenyl ring (cf. Figure 4) (*27*). Most of these compounds have been identified in soot and smoke condensate from residential wood stoves and were proposed as tracers for this fugitive source (*21–24*). Both hard- and softwoods produced guaiacol [2-(methylox)phenol] derivatives in the smoke, whereas hardwood in addition produced high levels of syringol (1,3-dimethoxyphenol) derivatives (*22, 23*). Hawthorne et al. (*23*) concluded that guaiacyl derivatives are potential tracers for both types of wood smoke, and syringyl derivatives indicate an input from hardwood smoke. A detailed evaluation of the source strengths of smoke emissions from combustion of hard- and softwoods in stoves has been presented (*22, 23*), but the long-term atmospheric stability of these products remains to be evaluated.

The lignin pyrolysis products are major compounds in the fine aerosol fraction of the smoke samples used in the

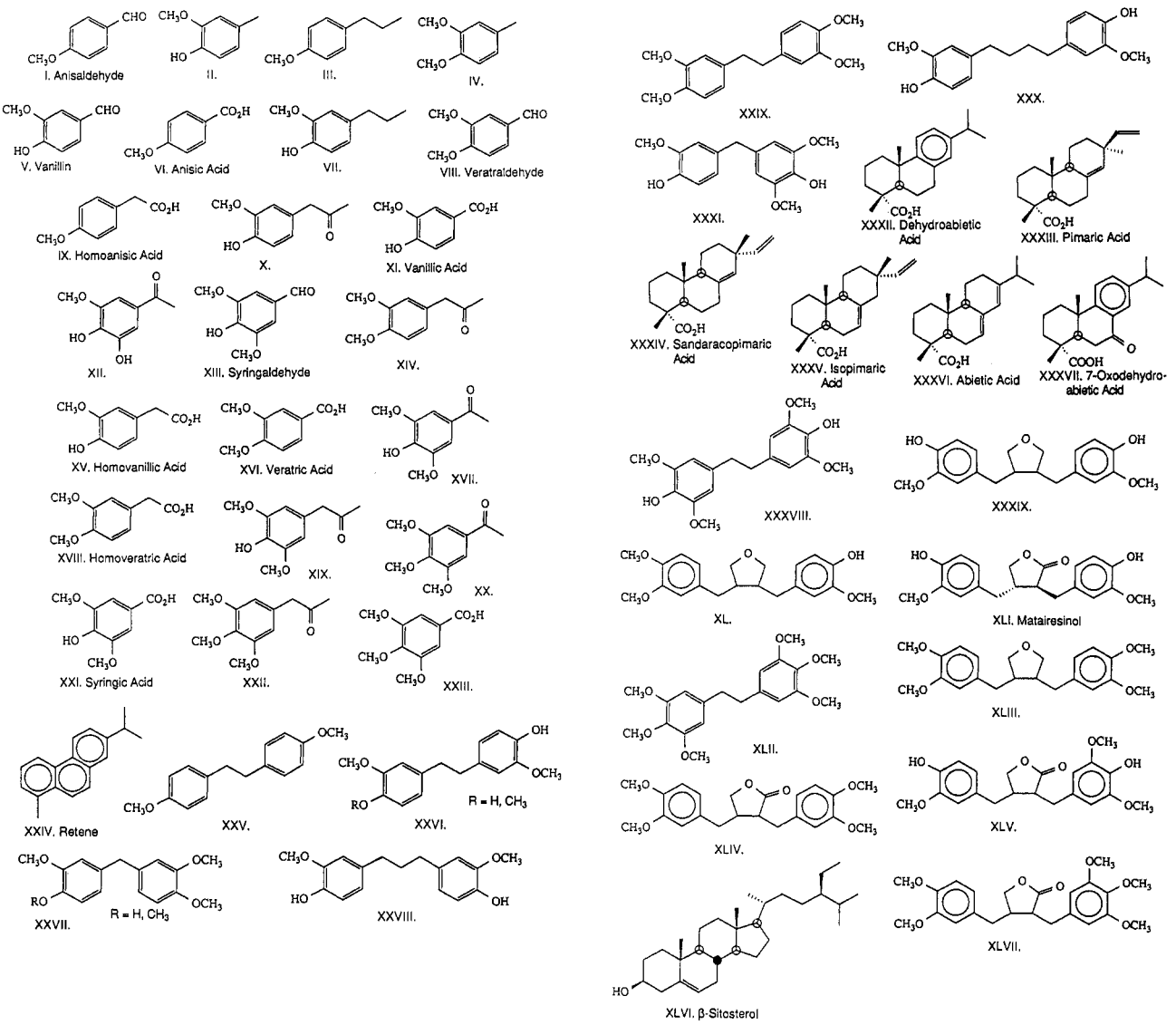

Figure 2. Chemical structures cited in the text and Table I.

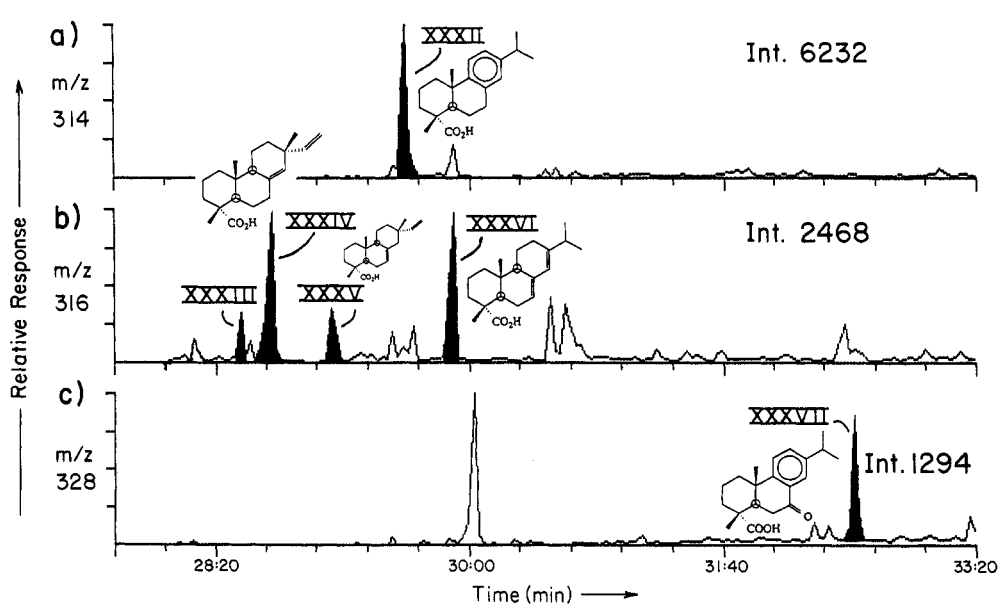

Figure 3. Salient features for the molecular ions of the diterpenoid acids in the GC/MS data for the total extracts of fine particles from pine wood smoke. Roman numerals refer to Table I and Figure 2; Int, relative intensity of ion.

present study from fires burning wood or grass. Pine wood smoke contains mainly vanillin (**V**) and vanillic acid (**XI**; Figure 1, Table I) and lesser amounts of other pyrolysis products from coniferyl-type lignin (e.g., **II**, **IV**, **VII**, **X**,

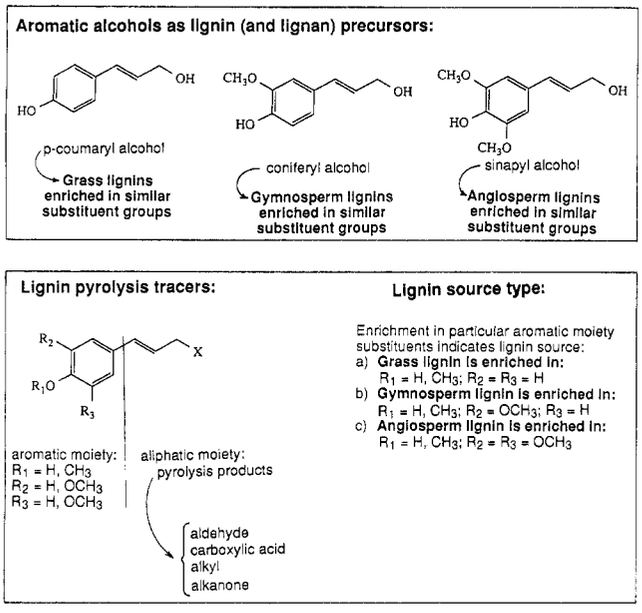

Figure 4. Schematic of the biochemical precursors for lignin and lignans, of lignin pyrolysis products as tracers and source types, and of the lignan sources.

XIV, and **XV**; Figure 1, Table I), as would be expected from gymnosperm lignin. However, minor amounts of syringaldehyde (**XIII**) and syringic acid (**XXI**) as well as *p*-anisic acid (**VI**) (Figure 1) are also detectable. These same compound proportions were reported in soot and condensate from wood smoke by Hawthorne et al. (*22*), but no extensive connection was made between the natural product composition of the underlying taxa and the distribution of the products in the wood smoke. From the present experiments, we can see that oak wood smoke is enriched in syringaldehyde (**XIII**) and syringic acid (**XXI**) and various amounts of the sinapyl-type and other lignin pyrolysis products (e.g., **II**, **IV**, **VII**, **XVI**, **XVII**, **XIX**, **XX**, and **XXII**; Figure 1, Table I), consistent with angiosperm lignin as the source, although lesser amounts of vanillyl-type products are also present. Grass smoke contains primarily *p*-anisaldehyde (**I**) and *p*-anisic acid (**VI**) (note—these compounds occur as *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid in the smoke and are methylated during derivatization prior to analysis) and minor amounts of other *p*-coumaryl-type lignin pyrolysis products (e.g., **III** and **IX**; Table I). While the presence of single vanillyl-, syringyl-, or coumaryl-type compounds in a smoke or aerosol sample does not constitute a unique tracer for the original source of biomass that was burned, the relative proportions of such compounds can be used to identify the nature of the underlying fuel. The differentiation of hard- and softwood smoke based on syringol derivatives has already been demonstrated (*22*).

(iv) Lignans. Many woody plants are enriched in lignans (Figures 4 and 5), which are basically dimers of *p*-coumaryl, coniferyl, and sinapyl alcohols (e.g., refs 71–76). The "dimers" reported by Goñi and Hedges (*77*) in CuO oxidation products are not equivalent to the lignan natural products. Lignans serve the plants as toxins, as supportive filler, and for other purposes (*68*, *78*). Lignans are present as significant components in the smoke from pine wood (Figure 1a), are less prominent in the oak wood

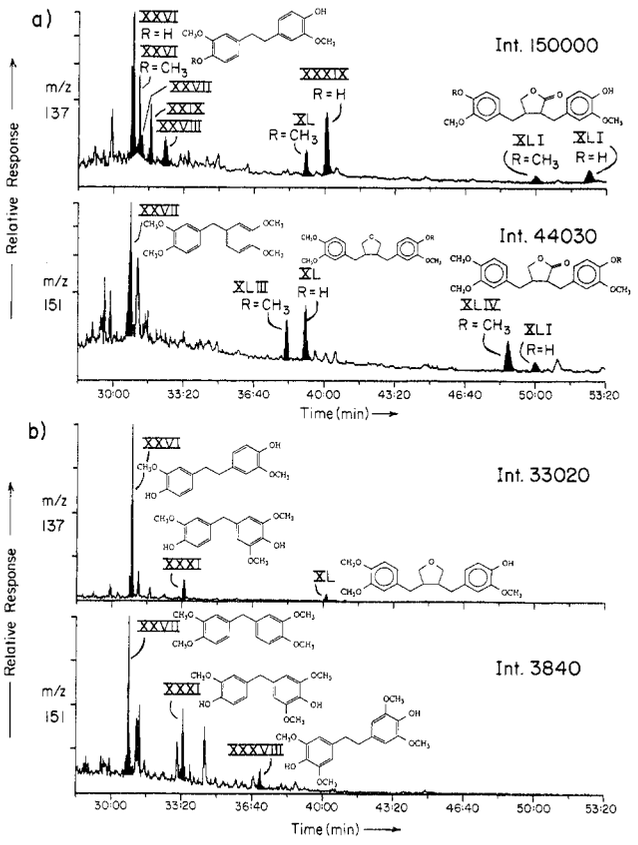

Figure 5. Mass fragmentograms showing the key ions. Note these ions are not the base peaks for all compounds detected, e.g., **XLI**, R = H, **XXXI**, and **XXXVIII**, for the dominant lignans and phenol dimers in (a) pine wood smoke and (b) oak wood smoke. Roman numerals refer to Table I and Figure 2; Int, relative intensity of ion.

smoke (Figure 1b), and are not detectable in grass smoke. The predominant lignans are indicated in the mass fragmentograms of their key ions from the GC/MS data (Figure 5) and are listed in Table I. The major lignans of pine wood smoke are matairesinol (**XLI**) and tetrahydro-3,4-divanillylfuran (**XXXIX**), with lesser amounts of various methylated derivatives (i.e., **XL**, **XLIII**, and **XLIV**). Oak smoke contains various isomers of dihydro-vanillylsyringyl-2(3*H*)-furanone (**XLV**), dihydro-3(2′,3′,4′-trimethoxyphenyl)-4-veratryl-2(3*H*)-furanone (**XLVII**), and tetrahydro-3-vanillyl-4-veratrylfuran (**XL**). These highly oxygenated compounds are injected unaltered into the smoke and may also be useful tracers for wood combustion.

An additional group of compounds present in smoke from pine wood, oak wood, and grass can be interpreted to be secondary dimer compounds derived by radical recombination from pyrolysis products of lignin, although a primary origin as natural products cannot be excluded. These compounds are assigned as the following structures on the basis of the interpretation of their fragmentation patterns in the GC/MS data (Table I), and three such compounds were also reported by Hawthrone et al. (*22*) in wood smoke.

Pine wood smoke contains mainly divanillyl (**XXVI**, i.e., 1,2-diguaiacylethane; ref 22), divanillylmethane (**XXVIII**), divanillylethane (**XXX**), and minor amounts of bis-(3,4-dimethoxyphenyl)methane (**XXVII**) and diveratryl (**XXIX**). All these compounds are derived from coniferyl-type precursors.

Oak wood smoke has the following compounds of this group derived from sinapyl-type precursors: bisguaiacyl-syringyl (**XXXI**), disyringyl (**XXXVIII**, i.e., 1,2-disyringylethane; ref 22), and bis(3,4,5-trimethoxyphenyl)-ethane (**XLII**, not shown in Figure 5); and divanillyl (**XXVI**) and bis(3,4-dimethoxyphenyl)methane (**XXVII**) derived from coniferyl-type precursors.

The grass smoke studied has only one of these compounds, namely, dianisyl (**XXV**), derived from a *p*-coumaryl-type precursor.

The lignans and secondary dimers have generally the same substituent pattern (OH, OCH_3) on the aromatic rings as the precursor aromatic alcohols from which they were derived. The relative proportions of these precursors in the parent plant material are reflected in the relative proportions of the substituents found on the lignans and secondary phenol dimers. This pattern in turn can be used to help identify the plant class of the biomass fuel being combusted. Thus, these compounds complement the lignin pyrolysis products in the application of the tracer concept for source strength assessment in biomass combustion. Extracts of the fine fraction of various urban aerosol samples from Los Angeles during the winter (1982) had elevated levels of resin acids (*36*) and were examined for the presence of lignans and phenol dimers (*42*). The major phenolic compounds that have been identified there are matairesinol (**XLI**), tetrahydro-3,4-divanillylfuran (**XXXIX**), and divanillyl (4,4′-dihydroxy-3,3′-dimethoxybibenzyl, **XXVI**). These are the same compounds which are found primarily in pine wood smoke, lending support to earlier data (*79*) indicating that ~80% of the organic carbon emitted from fireplaces in the Los Angeles basin originates from combustion of soft wood.

(v) Molecular Tracers of Major Vegetation Classes. The resin acids (diterpenoid acids, **XXXII–XXXVII**) are specific tracers for conifer vegetation or for products manufactured from conifer material (e.g., resin-containing industrial materials). Since these compounds are predominant in the resin of conifer wood and are not common in the epicuticular wax (e.g., ref 56), their injection into the atmosphere is typically by direct volatilization (distillation) during wood combustion. Therefore, the presence of resin acids, especially dehydroabietic acid (**XXXII**) accompanied by significant concentrations of unaltered resin acids such as structures **XXXIII–XXXVI**, in aerosols can be used as an indicator for wood smoke from gymnosperms.

Phytosterols (mainly C_{29}) are useful tracers to confirm the presence of particle sources from vegetation. The full range of possibilities for injection of phytosterols into the atmosphere is not yet defined completely. They are present in wood smoke but are also found in epicuticular waxes of many plant species (*56, 80*).

Both the lignin pyrolysis products and lignans in smoke from biomass combustion convey source information. The phenolic substitution pattern on the benzylic moiety of these molecules is characteristic of the plant class (cf. Figure 4). In general, grass lignin is enriched in products biosynthesized from *p*-coumaryl alcohol, gymnosperm lignins and lignans are enriched in products biosynthesized from coniferyl alcohol and from lesser amounts of other phenolic alcohols, and angiosperm lignins and lignans are enriched in products biosynthesized from sinapyl alcohol with significant incorporation of other phenolic alcohols. The relative abundances of the functional group substitution patterns on the aromatic moieties of the lignin pyrolysis products, the secondary dimers (e.g., **XXV–XXXI, XXXVIII**, and **XLII**), and the lignans found in wood or grass smoke reflect the underlying biosynthetic process characteristic of each plant class and can be utilized as potential indicators for the type of plant material that was burned during biomass combustion.

Conclusions

In order to assess and trace combustion aerosols from biomass fires, it is useful to identify characteristic marker compounds which can be used to distinguish between the different types of biomass sources that have been burned (e.g., grass fires, forest fires, conifers vs deciduous trees, etc.). Here thermally unaltered and partially altered organic tracers in smoke from major vegetation taxa have been identified. The smoke aerosol biomarkers encompass a carbon range of C_8–C_{31} and include phenolic products from lignin precursors, lignans, phytosterols, and resin constituents. Manyof these compounds are present in significant concentrations in the smoke aerosols to make their detection and quantitation by mass spectrometric methods relatively easy.

The biomarker compounds found in wood and grass smoke aerosols are formed by two different mechanisms: by direct vaporization and by pyrolytic catalysis involving some alteration and possibly dimer formation. In both cases, it is possible to assign many of these molecules to the unburned biofuel. The diterpenoid acids are notably good indicators of wood smoke from gymnosperms since these resinous components are found thermally unaltered in the smoke aerosol and are present in large abundance. The lignin pyrolysis products, lignans, and phenol dimers are also major compounds in the fine aerosol fractionof burned wood or grass. These pyrolytic molecular tracers are oxygenated, polar aromatic compounds and generally have a substituent pattern (OH, OCH_3) on their aromatic rings that reflects the mixture of precursor aromatic alcohols which is characteristic of the plant class of the biomass source. Thus, it is possible to distinguish the relative abundance of coniferyl-, sinapyl-, and *p*-coumaryl-type lignin precursors, together with lignans and resin components, found in wood smoke mixtures. These relative abundances in turn can be used as a guide to the relative amounts of conifer, hardwood, and grass smoke present. A qualitative comparison of wood smoke samples to existing data on the ambient concentrations of lignans and resin compounds in the Los Angeles atmosphere is encouraging. Both the ambient tracer data and the prior surveys of local wood use suggest that pine is the dominant wood burned in fireplaces of that area.

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