



Molecular characterization of smoke from campfire burning of pine wood (*Pinus elliottii*)

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Importance of this paper: The combustion conditions of wood burned in campfires are different from those of indoor wood burning in stoves or fireplaces. For human exposure assessment, there is a need to fingerprint the organic compound compositions in campfire wood smoke. This is presented here. The major biomarker tracers are dehydroabietic acid, the resin acids (pimaric, iso-pimaric, sandaracopimaric and abietic acids), retene, pimanthrene, and methylcyclopentenophenanthrene, with β -sitosterol, levoglucosan and lignin methoxyphenols in the polar fraction. PAH are minor components.

Abstract

Although campfires are typically enjoyable events, people are exposed to high concentrations of gaseous and particulate pollutants. The combustion conditions of wood burned in campfires are different from those of indoor wood burning in stoves or fireplaces. Typically, wood logs, twigs, and branches with their leaves or needles are burned in campfires, whereas mostly wood logs are burned in indoor settings. Consequently, the molecular source profiles for organic particulate matter emissions may be different from a campfire. For human exposure assessment, there is a need to fingerprint the organic compound compositions in campfire wood smoke. Here we present the detailed biomarker composition of conifer wood smoke from a campfire. The major biomarkers emitted are dehydroabietic acid, the resin acids (pimaric, iso-pimaric, sandaracopimaric and abietic acids), retene, pimanthrene, methylcyclopentenophenanthrene and β -sitosterol, with levoglucosan and lignin phenolics such as vanillic acid in the polar fraction. PAH are minor components. A marker and PAH profile has been generated which can be utilized for tracing emissions from campfire burning and evaluating personal exposure risk. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Molecular markers; Pine smoke; Biomass burning; Resin acids; Organic aerosols; PAH; Source characterization

1. Introduction

Biomass burning has become a global concern and occurs on a large scale in industrialized, developing and remote areas caused both by anthropogenic and natural

initiation (wild fires). In urban and rural areas biomass, mainly wood, is burned for heating, cooking, waste disposal purposes and in the industrialized world even for aesthetic reasons in indoor fireplaces or campfires (e.g., Core et al., 1984; Freeman and Catell, 1990; Hawthorne et al., 1988; Lipfert and Dungan, 1983; Muhlbaier-Dasch, 1982; Ramdahl et al., 1984). All biomass fires are dominated by incomplete combustion processes causing polynuclear aromatic hydrocarbons

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(PAH) and aromatic biomarkers (biomarker PAH) to form from natural product precursors in the source organic matter (Simoneit, 1998). Wood combustion has been identified in earlier studies as a non-fossil fuel source (biofuel) that can contribute appreciably to the deterioration of both outdoor and indoor air quality (Core et al., 1984; Edye and Richards, 1991; Hawthorne et al., 1989, 1992; Honicky et al., 1985; Ramdahl et al., 1984; Rogge et al., 1998; Sexton et al., 1984; Standley and Simoneit, 1987). Previous studies were either focused on the characterization of wood smoke emissions from wild fires or on indoor wood burning in stoves or fireplaces. Due to their mutagenic and carcinogenic potential, PAH-type compounds were mainly analyzed in these emissions (Claessens and Lammerts van Bueren, 1987; Freeman and Cattell, 1990; Guenther et al., 1988; Kamens et al., 1984, 1985; Kleindienst et al., 1986; Ramdahl, 1983; Ramdahl and Becher, 1982).

1.1. Wood composition

Emissions from the combustion of any type of fuel depend directly on the chemical composition of the fuel and the combustion conditions. Different tree species develop markedly different woody constituents during growth and typically, all wood consists of various forms of lignins, celluloses and fillers (Pettersson, 1984). Cellulose provides a supporting mesh, which is reinforced by lignin polymers (~30% of woody tissue). The lignin biopolymers are derived from p-coumaryl, coniferyl and sinapyl alcohols and contain mainly anisyl, vanillyl and syringyl nuclei (Simoneit et al., 1993; Rogge et al., 1998). Tannins, terpenes and other compounds are the fillers in woody tissue making it a complex substance (Rogge et al., 1998). Many softwood species (gymnosperms) are prolific resin producers. The softwood genera, including pines (*Pinus*), spruces (*Picea*), larches (*Larix*), and firs (*Pseudotsuga*), have well-established systems of horizontal and vertical ducts filled with resin (Parham and Gray, 1984).

The moisture content of wood varies considerably and the optimal content in terms of minimizing particulate emissions during wood combustion is between 20% and 30% (Core et al., 1982). If the moisture content is too high, an appreciable amount of energy is necessary to vaporize the water, reducing the heating value of the wood as well as decreasing combustion efficiency, which in turn increases smoke formation (Core et al., 1982). This is a phenomenon often observed with campfires. On the other hand, wood with a low moisture content burns faster eventually causing oxygen-limited conditions that lead to incomplete combustion with increased wood smoke particle formation.

1.2. Wood combustion process

When wood is heated, its constituents start to hydrolyze, oxidize, dehydrate, and pyrolyze, and with increasing temperature form combustible volatiles, tarry substances, and highly reactive carbonaceous char (Shafizadeh, 1984). The exothermic reactions characteristic of wood combustion begin at the ignition temperature of the volatile and tarry substances. The heat release during flaming combustion first provides the energy necessary for gasification of the wood substrate and propagation of the fire, as well as evaporation of the “free or capillary water” found in the cell cavities, followed by the vaporization of bound water stored in the cell walls (Skaar, 1984). Together with the water, extractives such as resinous compounds and decomposition products of cellulose, hemicelluloses, and lignin are vaporized and can undergo further partial or complete combustion alteration in the flaming zone. During flaming combustion, char formation continues until the flux of combustible volatile substances drops below the minimum level required for the propagation of flaming combustion. Then the smoldering process starts and is best described as the gradual oxidation of the reactive char (solid phase combustion). During the smoldering process in open fires too much heat is often lost to the surroundings causing the fire to extinguish itself. This is quite in contrast to stove fires where the heat stored in the wall radiates back causing the smoldering process to propagate to charring until all wood is consumed.

In contrast to wood burning in indoor stoves and fireplaces, both wet and dry wood, branches and needles are burned in campfires without any preselection. While the temperatures in indoor stoves and fireplaces are a function of the amount of fuel added and radiative heating caused by the confinement, campfire temperatures are typically lower and vary constantly due to blowing wind and the lack of radiative heating. Therefore, low temperature incomplete combustion is more often observed in campfires and consequently, the chemical composition of wood smoke aerosols from campfires show a higher degree of unburned and partially burned wood constituents than more confined indoor wood burning.

Here we present a detailed characterization of the organic compounds associated with smoke from a simulated campfire burning pine wood together with branches and needles.

2. Experimental methods

2.1. Sampling

Needles, twigs, branches and mainly wood of a dead and dry pine (*Pinus elliotii*, var. *densa*) were used

for the burn. The fuel was burned over a 3-h period. A Model 310 Universal Air Sampler (MSP, Minneapolis, MN) operated at 300 l/min was used for wood smoke sampling. Fine particulate matter with an aerodynamic diameter of less than 2.5 μm was collected on solvent precleaned glass fiber filters (CH_2Cl_2). In order to allow the wood smoke emissions to cool and dilute before sampling, the particle sampler was mounted on wheels and moved around the campfire at a distance of 3–5 m, depending on the wind direction. About 30–40 kg of fuel material was burned for the sampling period.

2.2. Extraction and fractionation

The filters were extracted with dichloromethane (CH_2Cl_2) for 24 h in a Soxhlet apparatus. The extract was concentrated on a rotary evaporator and then under a blow-down apparatus with nitrogen to about 2 ml. An aliquot of the total extract was analyzed directly after derivatization with silylating reagent. One quarter of the total extract was used for further fractionation. It was diluted with 30 ml of CH_2Cl_2 and the carboxylic acids were extracted with 20 ml 1 M sodium hydroxide solution. The organic layer with the neutral components was retained for further fractionation below, and the aqueous phase was acidified with HCl (preextracted with CH_2Cl_2) to $\text{pH} \leq 2$. The carboxylic acids were extracted with CH_2Cl_2 (20 ml), concentrated as above to 200 μl and derivatized with freshly prepared diazomethane. An internal standard (100 μg squalane) was added and the methyl ester fraction was concentrated to 200 μl for analysis.

The neutral extract fraction from the separation above was concentrated to 1 ml and applied to a liquid chromatography column filled with silica gel (7 g, 100–200 mesh). The following eight fractions were eluted

sequentially with the solvent mixtures indicated: F1 – 20 ml *n*-hexane, F2 – 15 ml hexane plus 5 ml toluene, F3 – 10 ml hexane plus 10 ml toluene, F4 – 19 ml hexane plus 1 ml ethyl acetate, F5 – 18 ml hexane plus 2 ml ethyl acetate, F6 – 17 ml hexane plus 3 ml ethyl acetate, F7 – 16 ml hexane plus 4 ml ethyl acetate, and F8 – 30 ml methanol. Fractions 3 and 4 were combined and 5 μg of internal standard added. All fractions were reduced to 100 μl prior to analysis. The internal standard (5 μg squalane) was also added to fractions 1 and 5. The total extract and fractions 6–8 were silylated after addition of the internal standard (F6, F7 – 5 μg , F8 – 10 μg squalane) by addition of 1 ml each of CH_2Cl_2 and BSTFA [bis(trimethylsilyl)trifluoroacetamide]. Each vial was heated at 40°C for 3 h, kept overnight and passed through a mini silica gel column prior to concentration for analysis.

2.3. Instrumental analyses

Gas chromatography (GC) was carried out with a Hewlett–Packard Model 5890A instrument equipped with a 30 m \times 0.25 mm capillary column coated with DB-5 and a flame ionization detector. The GC-mass spectrometry (MS) analyses were conducted with a Hewlett–Packard Model 5973 MSD quadrupole instrument, GC equipped with a 30 m \times 0.25 mm capillary column coated with DB-5 and data acquisition and processing station. Full mass spectra were acquired in the electron impact mode (70 eV) using a chemstation data system. The GC and GC-MS operating conditions for the column oven were the same: initial temperature 40°C for 1 min, program at 10°C/min to 150°C, then at 4°C/min to 280°C, and isothermal hold for 30 min. Compounds were identified from comparison with authentic standards, MS files, literature citations, and by interpretation of MS fragmentation patterns.

Table 1
Carbon number range and yields of compound groups in pine wood smoke particulate matter

Compound groups	Range	Total yield (μg)	Normalized yield ^a
<i>n</i> -alkanes	C ₁₈ –C ₃₃	10 340	20
<i>n</i> -alkenes	C ₁₈ –C ₃₁	20 200	39
PAH	C ₁₄ –C ₂₂	5550	11
Alkyl-PAH	C ₁₅ –C ₁₉	1620	3
Alkyl-PAH from terpenoids (e.g., retene)	C ₁₆ –C ₁₉	15 000	29
<i>n</i> -alkanoic acids	C ₁₂ –C ₂₈	7600	15
<i>n</i> -alkanols	C ₁₆ –C ₃₂	2174	4
Diterpenoids and derivatives	C ₁₇ –C ₂₀	52 000	100
Steroids	C ₂₈ –C ₂₉	11 100	21
Lignin pyrolysis phenols	C ₆ –C ₁₀	3800	7
Monosaccharide derivatives	C ₅ –C ₆	5100	10
Unknowns	–	1500	3
Total		135 984	

^a Normalized to diterpenoids, the major components of the total.

Table 2
Identities and yields of compounds present in various polarity fractions of extract from pine wood smoke particulate matter

Compound		Composition	MW ^a	Relative concentration (ng/g of total extract)	Structure (cf. Appendix A)	Identification basis or reference ^b
Number	Name					
<i>Aliphatic hydrocarbons (F1)</i>						
1	<i>n</i> -octadecane	C ₁₈ H ₃₈	254	50		A
2	<i>n</i> -nonadecane	C ₁₉ H ₄₀	268	140		A
3	<i>n</i> -eicosane	C ₂₀ H ₄₂	282	380		A
4	<i>n</i> -heneicosane	C ₂₁ H ₄₄	296	710		A
5	<i>n</i> -docosane	C ₂₂ H ₄₆	310	1380		A
6	<i>n</i> -tricosane	C ₂₃ H ₄₈	324	1670		A
7	<i>n</i> -tetracosane	C ₂₄ H ₅₀	338	1620		A
8	<i>n</i> -pentacosane	C ₂₅ H ₅₂	352	1290		A
9	<i>n</i> -hexacosane	C ₂₆ H ₅₄	366	2000		A
10	<i>n</i> -heptacosane	C ₂₇ H ₅₆	380	240		A
11	<i>n</i> -octacosane	C ₂₈ H ₅₈	394	190		A
12	<i>n</i> -nonacosane	C ₂₉ H ₆₀	408	430		A
13	<i>n</i> -hentriacontane	C ₃₁ H ₆₄	436	240		A
14	<i>n</i> -tritriacontane	C ₃₃ H ₆₈	464	190		A
15	<i>n</i> -octadec-1-ene	C ₁₈ H ₃₆	252	50		A
16	<i>n</i> -nonadec-1-ene	C ₁₉ H ₃₈	266	90		S
17	<i>n</i> -eicos-1-ene	C ₂₀ H ₄₀	280	240		A
18	<i>n</i> -heneicos-1-ene	C ₂₁ H ₄₂	294	480		S
19	<i>n</i> -docos-1-ene	C ₂₂ H ₄₄	308	670		S
20	<i>n</i> -tricos-1-ene	C ₂₃ H ₄₆	322	1570		S
21	<i>n</i> -tetracos-1-ene	C ₂₄ H ₄₈	336	8240		S
22	<i>n</i> -pentacos-1-ene	C ₂₅ H ₅₀	350	1760		S
23	<i>n</i> -hexacos-1-ene	C ₂₆ H ₅₂	364	5620		S
24	<i>n</i> -heptacos-1-ene	C ₂₇ H ₅₄	378	620		S
25	<i>n</i> -octacos-1-ene	C ₂₈ H ₅₆	392	190		A
26	<i>n</i> -nonacos-1-ene	C ₂₉ H ₅₈	406	430		S
27	<i>n</i> -hentriacont-1-ene	C ₃₁ H ₆₂	434	240		S
28	24-ethylcholesta-3,22-diene	C ₂₉ H ₄₈	396	950		S
29	24-methylcholesta-3,5-diene	C ₂₈ H ₄₆	382	380	XIV, R=CH ₃	A
30	24-ethylcholest-4-ene	C ₂₉ H ₅₀	398	710		S
31	24-ethylcholest-5-ene	C ₂₉ H ₅₀	398	760		S
32	24-ethylcholesta-4,6-diene	C ₂₉ H ₄₈	396	810		A
33	24-ethylcholesta-3,5-diene	C ₂₉ H ₄₈	396	3710	XIV, R=C ₂ H ₅	A
34	24-ethylcholesta-2,4-diene	C ₂₉ H ₄₈	396	810		S
	Total <i>n</i> -alkanes (CPI = 0.84)			10 340		
	Total <i>n</i> -alkenes (CPI = 0.35)			20 200		
<i>Aromatic hydrocarbons (F2–F4)</i>						
35	Phenanthrene	C ₁₄ H ₁₀	178	360		A
36	Anthracene	C ₁₄ H ₁₀	178	36		A
37	3-methylphenanthrene	C ₁₅ H ₁₂	192	80		A
38	2-methylphenanthrene	C ₁₅ H ₁₂	192	212		A
39	9-methylphenanthrene	C ₁₅ H ₁₂	192	440		A
40	1-methylphenanthrene	C ₁₅ H ₁₂	192	108		A
41	Dimethylphenanthrenes	C ₁₆ H ₁₄	206	780		A
42	Pimanthrene	C ₁₆ H ₁₄	206	1676	XVII	A
43	Fluoranthene	C ₁₆ H ₁₀	202	828		A
44	Acephenanthrylene	C ₁₆ H ₁₀	202	512		A
45	Pyrene	C ₁₆ H ₁₀	202	832		A
46	Trimethylphenanthrenes	C ₁₇ H ₁₆	220	1880		S
47	Norsimonellite	C ₁₈ H ₂₂	238	1084		S
48	Cyclopentenophenanthrene	C ₁₇ H ₁₄	218	584		I
49	Cyclopentenophenanthrene	C ₁₇ H ₁₄	218	636		I
50	Dihydroretenes	C ₁₈ H ₂₀	236	1144		I

Table 2 (Continued)

Compound		Composition	MW ^a	Relative concentration (ng/g of total extract)	Structure (cf. Appendix A)	Identification basis or reference ^b
Number	Name					
51	18-norabieta-6,8,11,13-tetraene	C ₁₉ H ₂₆	254	120		I
52	Dehydroabietin	C ₁₉ H ₂₈	256	268	XVIII	A
53	Dehydroabietane	C ₂₀ H ₃₀	270	322	XIX	A
54	Retene	C ₁₈ H ₁₈	234	4488	XV	A
55	Methylretene	C ₁₉ H ₂₀	248	948		S
56	Methylcyclopentenophenanthrene	C ₁₈ H ₁₆	232	2312	XVI	I
57	Simonellite	C ₁₉ H ₂₄	252	720	XX	A
58	Benzo[ghi]fluoranthene	C ₁₈ H ₁₀	226	384		A
59	Cyclopenta[cd]pyrene	C ₁₈ H ₁₀	226	380		S
60	Benz[a]anthracene	C ₁₈ H ₁₂	228	468		A
61	Chrysene/triphenylene	C ₁₈ H ₁₂	228	456		A
62	Methyl 228 PAH	C ₁₉ H ₁₄	242	60		I
63	Methyl 228 PAH	C ₁₉ H ₁₄	242	132		I
64	Dimethylcyclopentenophenanthrene	C ₁₉ H ₁₈	246	104		I
65	Benzo[b/k]fluoranthene	C ₂₀ H ₁₂	252	312		A
66	Benzo[e]pyrene	C ₂₀ H ₁₂	252	148		A
67	Benzo[a]pyrene	C ₂₀ H ₁₂	252	208		A
68	Perylene	C ₂₀ H ₁₂	252	76		A
69	Indeno[1,2,3-cd]pyrene	C ₂₂ H ₁₂	276	148		A
70	Benzo[ghi]perylene	C ₂₂ H ₁₂	276	104		A
71	Unknown		396	184		I
72	19-nor-24-ethylcholesta-1,3,5(10)-triene	C ₂₈ H ₄₄	380	144		I
73	Unknown		396	544		I
	Total PAH			5548		
<i>Carboxylic acids</i>						
74	<i>n</i> -dodecanoic acid	C ₁₂ H ₂₄ O ₂	200	450		S
75	<i>n</i> -tetradecanoic acid	C ₁₄ H ₂₈ O ₂	228	170		S
76	<i>n</i> -pentadecanoic acid	C ₁₅ H ₃₀ O ₂	242	170		S
77	<i>n</i> -hexadecanoic acid	C ₁₆ H ₃₂ O ₂	256	460		A
78	<i>n</i> -heptadecanoic acid	C ₁₇ H ₃₄ O ₂	270	57		S
79	<i>n</i> -octadecanoic acid	C ₁₈ H ₃₆ O ₂	284	570		S
80	<i>n</i> -eicosanoic acid	C ₂₀ H ₄₀ O ₂	312	514		S
81	<i>n</i> -docosanoic acid	C ₂₂ H ₄₄ O ₂	340	628		S
82	<i>n</i> -tetracosanoic acid	C ₂₄ H ₄₈ O ₂	368	2116		S
83	<i>n</i> -hexacosanoic acid	C ₂₆ H ₅₂ O ₂	396	2159		S
84	<i>n</i> -octacosanoic acid	C ₂₈ H ₅₆ O ₂	424	286		S
85	α,ω -hexadecanedioic acid	C ₁₆ H ₃₀ O ₄	286	280		A
86	α,ω -docosanedioic acid	C ₂₂ H ₄₂ O ₄	370	10		S
87	15,16,17-trisnordehydroabietic acid	C ₁₇ H ₂₂ O ₂	258 (330)	300	XIII, R=H	S, I
88	Trans-9-(3'-isopropylphenyl)-2,6-dimethyl-6-nonenoic acid	C ₂₀ H ₃₀ O ₂	302 (374)	286	XI	S, 2
89	5 α (H)-9,10- <i>seco</i> -dehydroabietic acid	C ₂₀ H ₃₀ O ₂	302 (374)	228	XII	S, 2
90	16,17-bisnordehydroabietic acid	C ₁₈ H ₂₄ O ₂	272 (344)	320	XIII, R=CH ₃	A
91	8,15-pimaradien-18-oic acid	C ₂₀ H ₃₀ O ₂	302 (374)	1827	VI	A
92	Pimaric acid	C ₂₀ H ₃₀ O ₂	302 (374)	2684	IV	A
93	Sandaracopimaric acid	C ₂₀ H ₃₀ O ₂	302 (374)	1142	V	A
94	Iso-pimaric acid	C ₂₀ H ₃₀ O ₂	302 (374)	10 366	II	A

Table 2 (Continued)

Compound		Composition	MW ^a	Relative concentration (ng/g of total extract)	Structure (cf. Appendix A)	Identification basis or reference ^b
Number	Name					
95	Methyl dehydroabietate	C ₂₁ H ₃₀ O ₂	314	1700	I	A
96	Abieta-6,8,11,13-tetraen-18-oic acid	C ₂₀ H ₂₆ O ₂	298	4060	VIII	A
97	Dehydroabietic acid	C ₂₀ H ₂₈ O ₂	300 (372)	23 884	I	A
98	Abietic acid	C ₂₀ H ₃₀ O ₂	302 (374)	3886	III	A
99	Abieta-6,8,11,13,15-pentaen-18-oic acid	C ₂₀ H ₂₄ O ₂	296 (368)	200		A, 1
100	12-methylthiodydroabietic acid	C ₂₁ H ₃₀ OS	346 (418)	150		I
101	Abieta-8,11,13,15-tetraen-18-oic acid	C ₂₀ H ₂₆ O ₂	298 (370)	3140	VII	A, 1
102	7-oxoabieta-5,8,11,13-tetraenoic acid	C ₂₀ H ₂₄ O ₃	312 (384)	288	X	S, I
103	7-oxodehydroabietic acid	C ₂₀ H ₂₆ O ₃	314 (386)	1006	IX	A
104	3-hydroxypimaric acid	C ₂₀ H ₃₀ O ₃	318 (462)	280		I
105	Octadec-9-enoic acid	C ₁₈ H ₃₄ O ₂	282	170		A
	Total <i>n</i> -alkanoic acids			7480		
	Total resin acids			57 740		
<i>Ketones</i> (F5 and F6)						
106	Nordehydroabietal	C ₁₉ H ₂₆ O	270	280	XXI	I
107	Dehydroabietal	C ₂₀ H ₂₈ O	284	466	XXII	A
108	7-oxoabiet-13-ene	C ₂₀ H ₃₂ O	296	210		I
109	3-oxoabieta-6,8,11,13-tetraene	C ₂₀ H ₂₆ O	290	70		I
110	Benzofluorenone	C ₁₇ H ₁₀ O	230	233		A
111	Campesterone	C ₂₈ H ₄₆ O	398	70	XXIV, R=CH ₃	A
112	Sitosterone	C ₂₉ H ₄₈ O	412	578	XXIV, R=C ₂ H ₅	A
113	24-ethylcholesta-4,6-dien-3-one	C ₂₉ H ₄₆ O	410	233	XXV	S
<i>Alcohols</i> (F6–F8)						
114	<i>n</i> -hexadecanol	C ₁₆ H ₃₄ O	242	83		S
115	<i>n</i> -docosanol	C ₂₂ H ₄₆ O	326	66		A
116	<i>n</i> -tetracosanol	C ₂₄ H ₅₀ O	354	1163		S
117	<i>n</i> -pentacosanol	C ₂₅ H ₅₂ O	368	64		S
118	<i>n</i> -hexacosanol	C ₂₆ H ₅₄ O	382	750		S
119	<i>n</i> -octacosanol	C ₂₈ H ₅₈ O	410	23		S
120	<i>n</i> -triacontanol	C ₃₀ H ₆₂ O	438	5		S
121	<i>n</i> -dotriacontanol	C ₃₂ H ₆₆ O	466	20		S
	Total <i>n</i> -alkanols			2174		
122	Abietol	C ₂₀ H ₃₂ O	288 (360)	650	XXIII	I
123	Abietol	C ₂₀ H ₃₂ O	288 (360)	790	XXIII	I
124	Pimarol	C ₂₀ H ₃₂ O	288 (360)	220		I
125	Methylpodocarpol	C ₁₈ H ₂₆ O	258 (330)	167		I
126	Dehydroabietol	C ₂₀ H ₃₀ O	286 (358)	626	XXVI	I
127	15-hydroxydehydroabietic acid	C ₂₀ H ₂₈ O ₃	316 (402)	83	XXVII	A, 3

Table 2 (Continued)

Compound		Composition	MW ^a	Relative concentration (ng/g of total extract)	Structure (cf. Appendix A)	Identification basis or reference ^b
Number	Name					
128	Campesterol	C ₂₈ H ₄₈ O	400 (472)	125	XXVIII, R=CH ₃	A
129	Stigmasterol	C ₂₉ H ₄₈ O	412 (484)	40	XXIX	A
130	β-sitosterol	C ₂₉ H ₅₀ O	414 (486)	1733	XXVIII, R=C ₂ H ₅	A
131	β-sitostanol	C ₂₉ H ₅₂ O	416 (488)	42	XXX	S
132	Unknown		372 (370?)	178		
133	Unknown		382 (384?)	60		
<i>Phenols (Lignin pyrolysis)</i>						
134	Catechol	C ₆ H ₆ O ₂	110 (234)	500		A
135	Dihydroxytoluene	C ₇ H ₈ O ₂	124 (268)	200		S
136	Vanillic acid	C ₈ H ₈ O ₄	168 (312)	1080	XXXI	A
137	Vanillyl ethanol	C ₁₀ H ₁₄ O ₃	182 (326)	1350	XXXII	A
138	Vanillyl acetic acid	C ₁₀ H ₁₂ O ₄	196 (340)	630	XXXII	A
<i>Monosaccharide derivatives</i>						
139	Arabinopyranose	C ₅ H ₁₀ O ₅	150	700		I
140	Methyl mannofuranoside			1000		I
141	Levoglucosan isomer	C ₆ H ₁₀ O ₅	162 (378)	900		S
142	Levoglucosan	C ₆ H ₁₀ O ₅	162 (378)	2400	XXXIV	A

^a Molecular weight (as trimethylsilyl derivative in parentheses).

^b Identification criteria: A = matches with authentic standard, S = interpolated from homologous series fragmentation pattern, I = interpreted from mass spectrum fragmentation pattern. Numbers refer to literature citation for example of authentic mass spectrum (generally not in the MS library): 1 – Anderson and Botto (1993); 2 – Beck et al. (1994) and Takeda et al. (1968); 3 – Franich and Holland (1985).

3. Results and discussion

3.1. Compound identification

The carbon number range and yields of compound groups in the pine wood smoke particles are given in Table 1. The identities and yields of individual compounds present in the various polarity fractions separated from the extract of pine wood smoke particles are summarized in Table 2.

(a) *Total extract composition*: An aliquot of the total extract was analyzed after silylation to elucidate the polar components derived from thermal breakdown of lignin and cellulose biopolymers. The total ion current

trace is shown in Fig. 1 and the numbers over the peaks refer to the compounds in Table 2.

The major compound is dehydroabietic acid (I, cf. Appendix A for chemical structures cited with Roman numerals), with lesser amounts of the other resin acids: iso-pimaric acid (II), abietic acid (III), pimaric acid (IV), sandaracopimaric acid (V), abieta-6,8,11,13-tetraen-18-oic acid (VIII), 8,15-pimaradienoic acid (VI), methyl dehydroabietate, abieta-8,11,13,15-tetraen-18-oic acid (VII), 15,16,17-trisnordehydroabietic acid (XIII, R=H), and 16,17-bisnordehydroabietic acid (XIII, R=CH₃). Traces of retene (XV), abieta-6,8,11,13,15-pentaen-18-oic acid, 12-methylthio-dehydroabietic acid and 3-hydroxypimaric acid are also

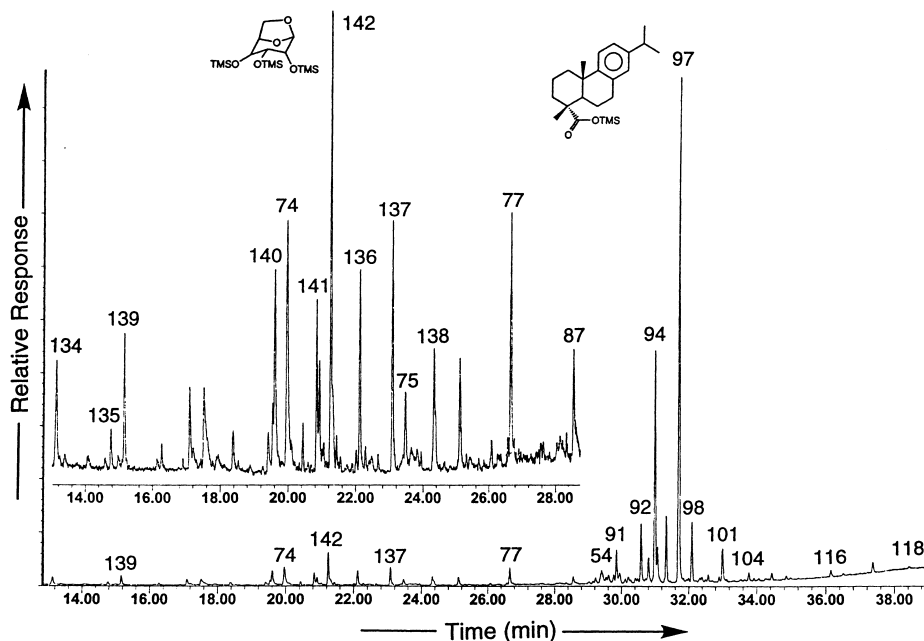


Fig. 1. Total ion current trace from GC-MS analysis of the total extract of pine smoke particles (derivatized with silylating reagent). Scale expansion by $10 \times$ for 12–29 min, numbers refer to compounds in Table 2.

detectable. The *n*-alkanoic acids, ranging from C_{12} to C_{18} are prominent.

The thermal degradation products from lignin are comprised of catechol (134, cf. Table 2), dihydroxytoluene (135), vanillic acid (136, XXXI), vanillyl ethanol (137, XXXII), and vanillyl acetic acid (138, XXXIII). The phenol substitution pattern is consistent with an origin from gymnosperm lignin enriched in coniferyl alcohol moieties (Simoneit et al., 1993). Lignans and secondary dimers were not detectable. Various monosaccharide products are present and can be interpreted to represent the thermal breakdown products from cellulose. The major compound which could be identified with an authentic standard is levoglucosan (1,6-anhydro- β -D-glucose, XXXIV, Simoneit et al., 1999).

(b) *Resin acids fraction*: The resin acids fraction contains the dominant compounds and the salient features of the GC-MS analysis are shown in Fig. 2. The major compound is dehydroabietic acid (I), with lesser amounts of iso-pimaric acid (II), abietic acid (III), pimaric acid (IV), sandaracopimaric acid (V) and 8,15-pimaradien-18-oic acid (VI). Other minor derivatives are abieta-8,11,13,15-tetraen-18-oic acid (VII), abieta-2 (or 1),8,11,13,-tetraen-18-oic acid (VIII), 7-oxodehydroabietic acid (IX), 7-oxoabieta-5,8,11,13-tetraenoic acid (X), trans-9-(3'-isopropylphenyl)-2,6-dimethyl-6-nonenic acid (XI, di-seco-dehydroabietic acid), 5 α (H)-9,10-seco-dehydroabietic acid (XII), 15,16,17-trisnordehydroabietic acid (XIII, R=H), and

16,17-bisnordehydroabietic acid (XIII, R=CH₃). Iso-pimaric, abietic, pimaric and sandaracopimaric acids are primary natural products occurring as such in resins, whereas compounds I and VI to XIII, especially dehydroabietic acid, are oxidative alteration products from the resin acids (Standley and Simoneit, 1994).

This fraction also contains the *n*-alkanoic acids which range from C_{12} to C_{28} , with a strong even carbon number predominance and C_{max} at C_{16} and C_{24} (Fig. 2(b)). The carbon preference index (CPI, Simoneit, 1978) of the *n*-alkanoic acids is 24.5. These acids have a similar high CPI as those in smoke from tropical vegetation (Abas et al., 1995) but with a different C_{max} . They are nevertheless not source specific. Trace amounts of dicarboxylic acids, namely C_{16} and C_{22} , and octadec-9-enoic acid are also present.

(c) *Neutral fraction*: The neutral fraction (non-polar) was further separated into eight subfractions prior to analysis. The compound yields are summarized in Table 2 and the relevant total ion current traces from the GC-MS analyses are shown in Fig. 3. Fraction 2 has a similar composition as combined fractions 3 and 4 (Fig. 3(b)); fraction 5 is similar to fraction 6 (Fig. 3 (c)), except the diterpenoid aldehydes are concentrated there; and fraction 8 shows only minor amounts of the same compounds present in fraction 7 (Fig. 3(d)).

The hydrocarbon fraction consists primarily of *n*-alk-1-enes (olefins) ranging from C_{18} to C_{28} with a CPI = 0.26 and C_{max} at C_{24} and C_{26} Fig. 3 (a). These

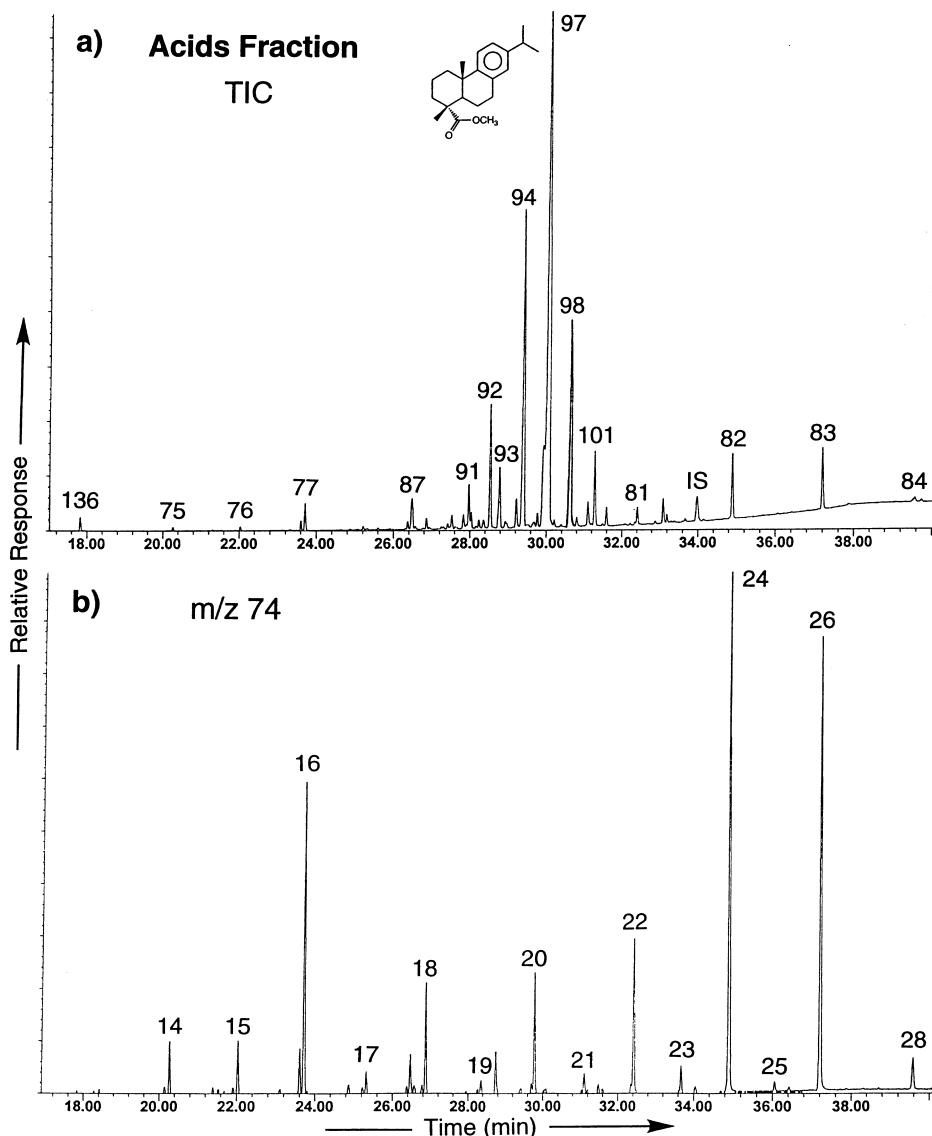


Fig. 2. Salient features of the GC-MS data for the carboxylic acid fraction (analyzed as methyl esters) from pine smoke particles: (a) Total ion current trace (numbers refer to compounds in Table 2), and (b) m/z 74 fragmentogram (key ion for methyl esters, numbers over peaks refer to carbon chain length of n -alkanoic acid, IS = internal standard).

alkenes are probably derived from both decarboxylation of n -alkanoic acids and dehydration of n -alkanols because the same C_{\max} is observed for both the n -alkanoic acid and the n -alkanol series in the lipid pool. Normal alkanes are also present ranging from C_{18} to C_{33} with a $CPI = 1.04$ and C_{\max} at C_{26} and C_{29} . The minor homologs $>n-C_{26}$ have a significant odd carbon number predominance, reflecting a quantitatively minor contribution of epicuticular wax alkanes from the pine needles ($CPI = 3.5 > C_{26}$) (Simoneit, 1989). A similar n -alkene/ n -alkane emission ratio was observed for smoke from tropical vegetation, thus making these compounds

non-source specific (Abas et al., 1995). Various hydrocarbon derivatives from the C_{28} and C_{29} phytosterols are present and consist of 24-ethylcholesta-3,5-diene (XIV $R=C_2H_5$) and minor amounts of 24-ethylcholesta-3,22-dienes, 24-methylcholesta-3,5-diene (XIV, $R=CH_3$), and 24-ethylcholestenes (Δ^4 and Δ^5). They are thermal dehydration products from the sterol precursors and can be used as general indicators for higher plant lipids (Simoneit, 1989).

The major compounds in fractions 2 and 3 plus 4 are retene (XV), methylcyclopentenophenanthrene (XVI), pimanthrene (XVII) and the polycyclic aromatic

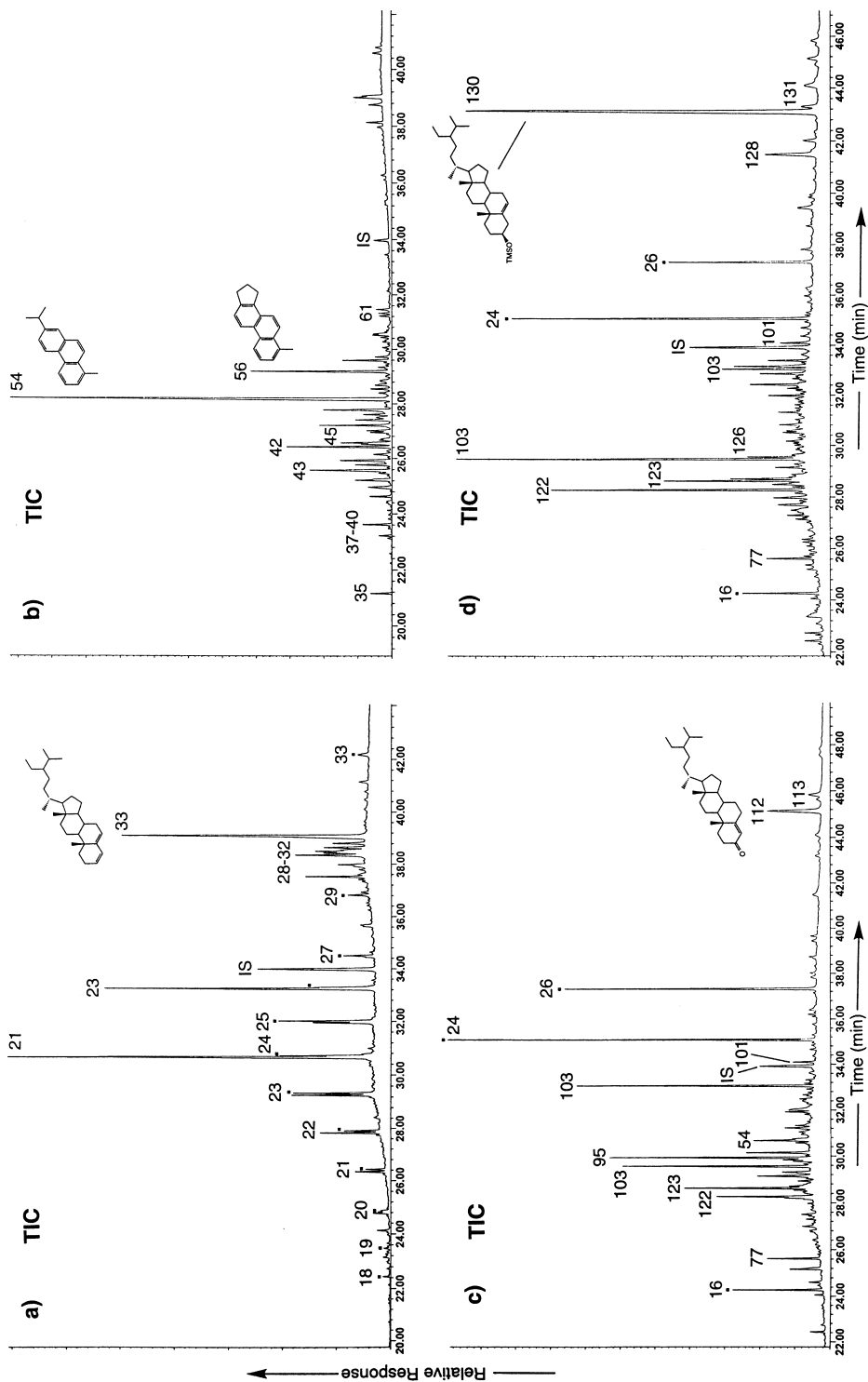


Fig. 3. Total ion current traces from GC-MS analyses of representative fractions separated from the non-acid extract fraction of pine smoke particles: (a) fraction 1, hydrocarbons, (b) combined fractions 3 and 4, aromatic hydrocarbons, (c) fraction 6, alcohols and ketones, and (d) fraction 7, alcohols (fractions 6 and 7 analyzed as silylated derivatives). Numbers refer to compounds in Table 2; numbers over dots on peaks are carbon chain length of alkanes/alkenes and alkanols; IS = internal standard.

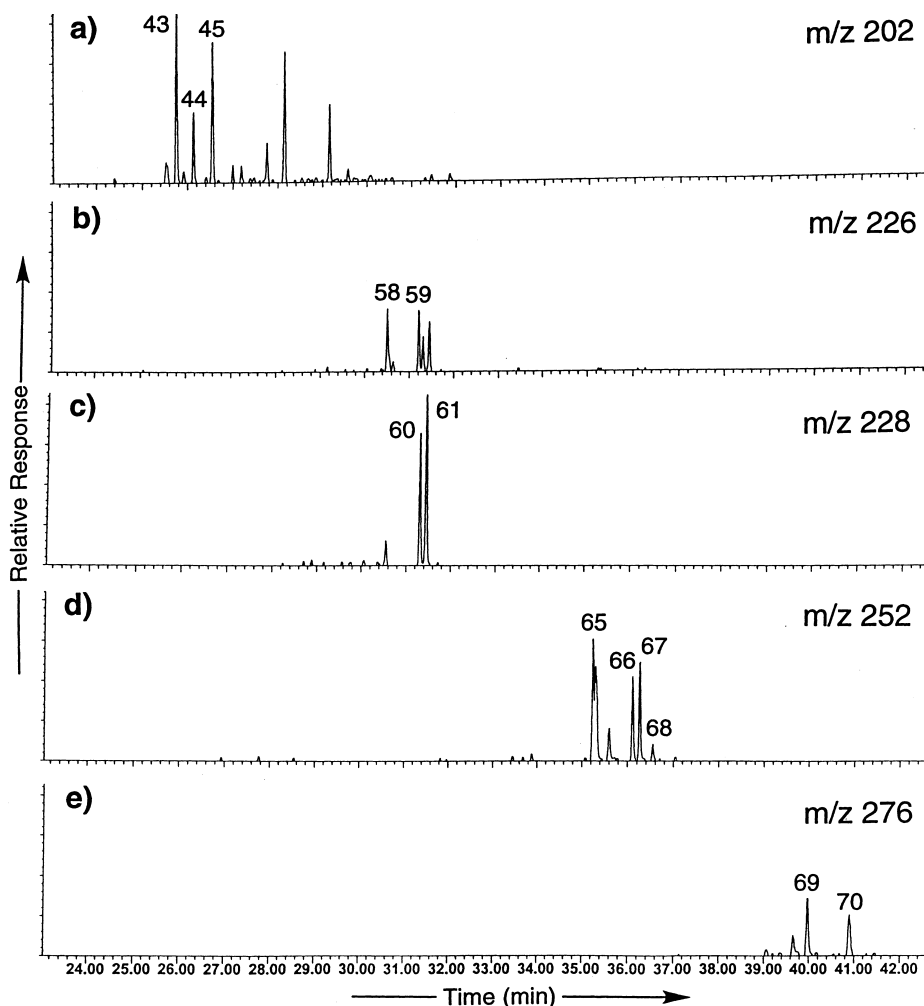


Fig. 4. Mass fragmentograms from GC-MS analysis of the aromatic hydrocarbons (fraction 3 plus 4): (a) m/z 202, (b) m/z 228, (c) m/z 226, (d) m/z 252, and (e) m/z 276 (numbers over peaks refer to compounds in Table 2).

hydrocarbons (PAH, e.g., Fig. 3(b)). Various other minor derivatives and intermediates from the resin acid precursors to the fully aromatic tricyclics are also present (e.g., dehydroabietin, XVIII, dehydroabietane, XIX, simonellite, XX, cyclopentenophenanthrene, etc.). The PAH are plotted separately for easier overview (Fig. 4) and are comprised mainly of the parent PAH (e.g., fluorenylene, pyrene, benzofluorene, cyclopenta[cd]pyrene, benz[a]anthracene, chrysene, methyl m/z 228 PAH, dimethylcyclopentenophenanthrene, benzofluoranthenes, benzopyrenes, perylene, indeno[1,2,3-cd] pyrene and benzo[ghi]perylene, see Table 2). The phenanthrene series is the exception, where the parent compounds, phenanthrene and anthracene, are present at trace levels and the alkyl series is enhanced, especially for C_2 and C_4 (i.e., pimanthrene and retene, Fig. 5). Thus, retene is a major hydrocarbon emitted in pine wood smoke as

reported earlier (Ramdahl, 1983; Hawthorne et al., 1992; Simoneit and Mazurek, 1982; Standley and Simoneit, 1990, 1994), however, additional aromatic hydrocarbon markers are also dominant.

The influence of combustion temperature, aeration, flaming combustion, and solid phase combustion (smoldering) on the formation of PAH is typically a factor of 10 higher for residential wood stoves than for residential fireplaces (Cooper, 1980). A similar lower PAH emission is observable for campfire wood burning, though an additional comparison study is necessary for quantitative conclusions.

The ketone fraction (F5, carbonyls) contains only minor amounts of nordehydroabietal (XXI), dehydroabietal (XXII) and 7-oxodehydroabietic acid (IX), with a significant carryover of dehydroabietic acid (I). The alcohols overlap from fractions 6–8. Fraction 6

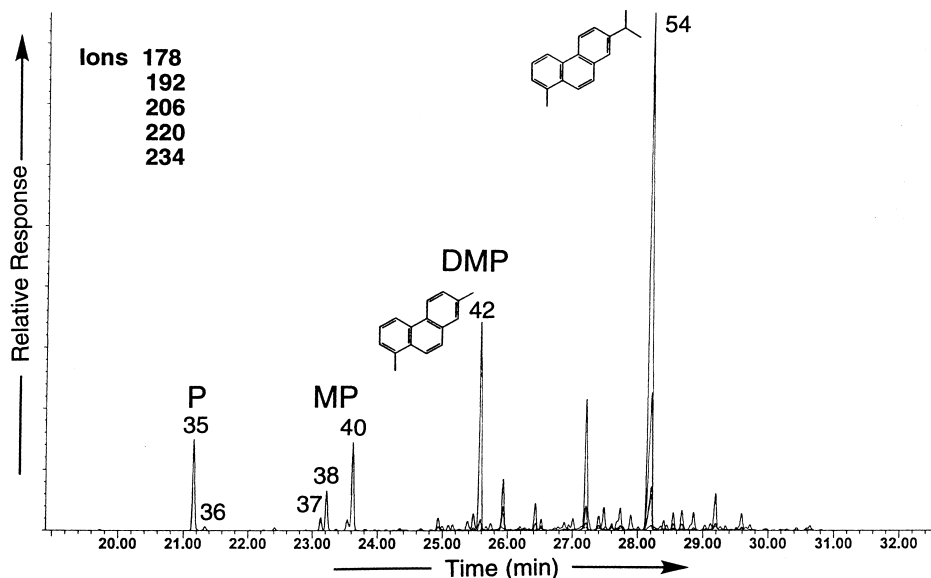


Fig. 5. Summed mass fragmentograms of m/z 178, 192, 206, 220 and 234 from GC-MS analysis of the aromatic hydrocarbons (fractions 3 plus 4) for the phenanthrene/anthracene series (numbers refer to compounds in Table 2, P=phenanthrene, MP=methylphenanthrenes, $C_2P=C_2$ homologs).

consists primarily of the *n*-alkanol series ranging from C_{16} to C_{23} with a CPI = 71 and C_{max} at C_{24} and C_{26} (Fig. 3(c)). Abiet-19-ol (XXIII) with other abietol isomers and various ketones, such as 7-oxodehydroabietic acid (IX), 7-oxoabieta-5,8,11,13-tetraenoic acid (X), campesterone (XXIV, $R=CH_3$), β -sitosterone (XXIV, $R=C_2H_5$) and 24-ethylcholesta-4,6-dien-3-one (XXV, $R=C_2H_5$), are also significant. The sterones are thermal oxidation products of the phytosterols. Fraction 7 (Fig. 3(d)) contains mainly various isomers of abietol (XXIII), dehydroabietol (XXVI), 15-hydroxydehydroabietic acid (XXVII), the phytosterols, and *n*-alkanols with the same range and C_{max} as in fraction 6. The phytosterols consist of primarily β -sitosterol (XXVIII, $R=C_2H_5$) with subordinate amounts of campesterol (XXVIII, $R=CH_3$), stigmasterol (XXIX), β -sitostanol (XXX) and β -sitosterone (XXIV, $R=C_2H_5$). β -Sitosterol is the principal phytosterol emitted in the smoke (Table 2). Fraction 8 consists primarily of alkanolic and diterpenoid acids from incomplete separation into the acids fraction and traces of phytosterols. No lignin phenols, lignans or other polar moieties described for total extract analyses (e.g., Simoneit et al., 1993; Rogge et al., 1983; Rogge et al., 1998) were detected in fraction 8.

3.2. Tracers for conifer smoke

The homologous compound series and biomarkers present in conifer smoke particles are derived directly from plant wax, gum and resin by volatilization and secondarily from pyrolysis of biopolymers (e.g., cellulose,

cutin, suberin, lignin), wax, gum and resin. The complexity of the organic components of the smoke aerosol were described in the previous section and here the specific tracers are discussed further.

The relationship of product to precursor alteration (both geological and thermal) for diterpenoids with the abietane skeleton has been presented by many authors (e.g., LaFlamme and Hites, 1979; Simoneit, 1977, 1986, 1998; Wakeham et al., 1980). This alteration commences with the dehydrogenation of abietic acid (III) to dehydroabietic acid (I), with subsequent decarboxylation to dehydroabietin (XVIII) and full aromatization to retene (XV). Dehydroabietane (XIX), which is found as the hydrocarbon in many resins, would dehydrogenate to simonellite (XX) and then proceed to retene. The various primaric acids (e.g., II, IV) have been shown to rearrange and also dehydrogenate to dehydroabietic acid or dealkylate and dehydrogenate to 16,17-bisnordehydroabietic acid (XIII, $R=CH_3$) which aromatizes to primanthrene (XVII) (Soltys, 1929; Grimalt et al., 1990; Standley and Simoneit, 1990, 1994). The tetracyclic kaurane and phyllocladane skeletons found in resins of *Podocarpaceae* and *Araucariaceae* of the Southern Hemisphere also rearrange under appropriate conditions to tricyclic products (Alexander et al., 1987, 1988). Kaurane and phyllocladane diterpenoids are, however, not significant components of conifer resin.

The major source specific biomarker compounds emitted in the pine smoke are dehydroabietic acid (I), and additional resin acids including: pimaric (IV), sandaracopimaric (V), iso-pimaric (II), and abietic (III)

acids, as well as aromatic hydrocarbons such as retene (XV), pimanthrene (XVII), and methylcyclopentophenanthrene (XVI). The intermediates such as dehydroabietin, dehydroabietane and simonellite mentioned above are minor components in this smoke sample. They may increase in concentration by secondary alteration of the numerous other minor compounds over time once in the atmosphere.

Additional specific biomarkers are observed in the total extract or the polar subfractions once those are silylated. These are various diterpenoid alcohols such as abietols (XXIII) and dehydroabietol (XXVI). The breakdown products from the lignin and cellulose biopolymers consist of characteristic phenolic and monosaccharide compounds (e.g., levoglucosan, XXXIV, Simoneit et al., 1999). The homologous series of *n*-alkanes, *n*-alk-1-enes, *n*-alkanoic acids and *n*-alkanols, and the PAH and phytosterols are not source specific because they are generally found in all biomass combustion emissions (e.g., Abas et al., 1995; Simoneit, 1984).

4. Conclusions

Smoke particulate matter from campfire burning of pine (*Pinus elliottii*) fuel contains a higher proportion of

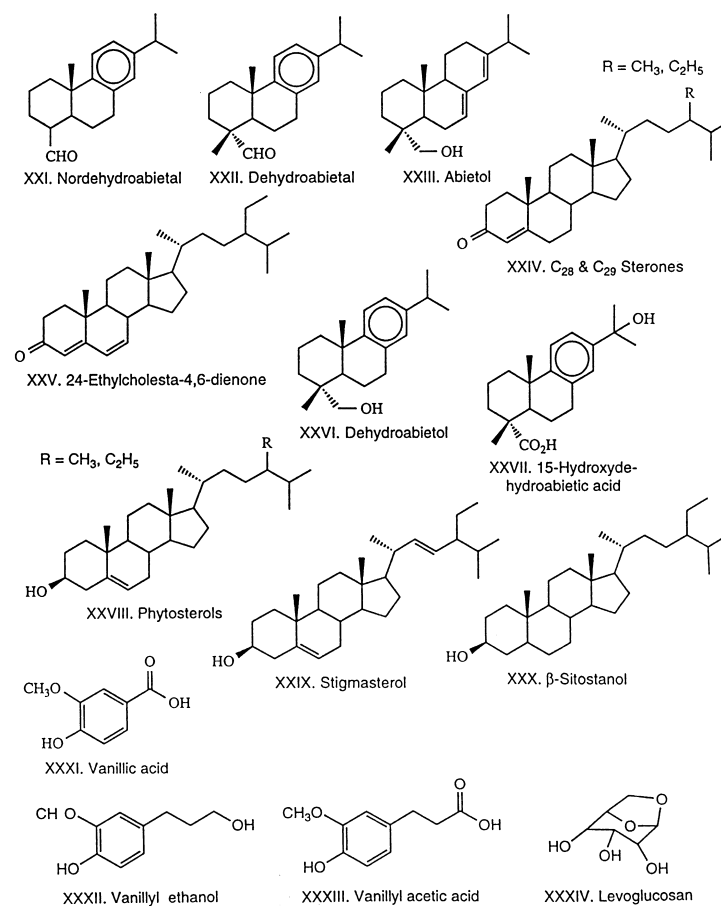
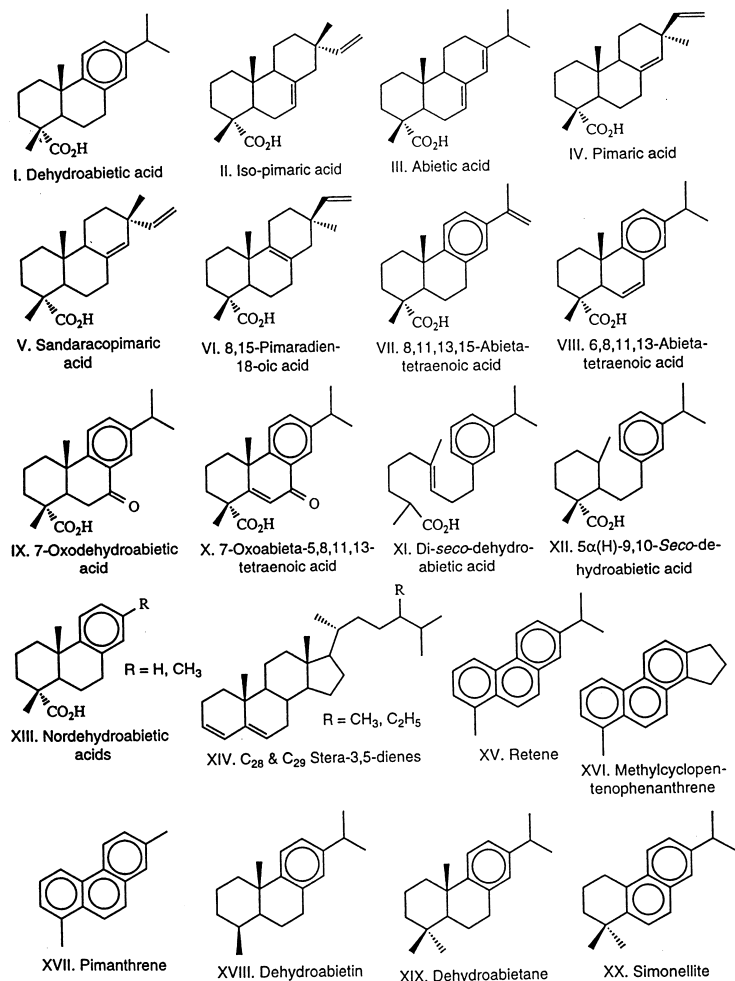
unaltered and partially altered diterpenoid tracers than completely pyrolyzed wood smoke constituents. The PAH content of smoke from campfire burning is lower compared to smoke from indoor wood burning (stoves or fireplaces). The major characteristic compounds are dehydroabietic acid, unaltered resin acids, retene, pimanthrene, and methylcyclopentophenanthrene in the neutral (hydrocarbon) and acid (methylated to esters for analysis) fractions. Polar tracers detectable in the total extract are levoglucosan and methoxyphenolics such as vanillic acid. Silylation of the more polar components revealed additional specific biomarkers such as abietol and dehydroabietol. The *n*-alkanes, *n*-alk-1-enes, *n*-alkanoic acids, *n*-alkanols, PAH and phytosterols are not specific because they are found in all biomass combustion emissions.

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Appendix A

Chemical structures cited.



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