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Methoxyphenols in Smoke from Biomass Burning

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Cover: Adsorbent sampling of smoke from the burning of birchwood. Photo: Marie Ullnert

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ABSTRACT

Wood and other forest plant materials were burned in laboratory experiments with the ambition to simulate the natural burning course in a fireplace or a forest fire. Smoke samples were taken and analysed with respect to methoxyphenols, using gas chromatography and mass spectrometry. Different kinds of biopellets, intended for residential heating were studied in the same way.

The aim of a first study was to establish analytical data to facilitate further research. Thirty-six specific methoxyphenols were identified, and gas chromatographic retention and mass spectrometric data were determined for these. In a subsequent study, the methoxyphenol emissions from the burning of wood and other forest plant materials were investigated. Proportions and concentrations of specific methoxyphenols were determined.

Methoxyphenols and anhydrosugars, formed from the decomposition of lignin and cellulose respectively, were the most prominent semi-volatile compounds in the biomass smoke. The methoxyphenol compositions reflected the lignin structures of different plant materials. Softwood smoke contained almost only 2-methoxyphenols, while hardwood smoke contained both 2-methoxyphenols and 2,6-dimethoxyphenols. The methoxyphenols in smoke from pellets, made of sawdust, bark and lignin, reflected the source of biomass.

Although smoke from incompletely burned wood contains mainly methoxyphenols and anhydrosugars, there is also a smaller amount of well-known hazardous compounds present.

The methoxyphenols are antioxidants. They appear mainly condensed on particles and are presumed to be inhaled together with other smoke components. As antioxidants, phenols interrupt free radical chain reactions and possibly counteract the effect of hazardous smoke components. Health hazards of small-scale wood burning should be re-evaluated considering antioxidant effects of the methoxyphenols.

Keywords: methoxyphenols, biomass, wood, lignin, smoke, combustion, antioxidants

List of publications

This work is based on the following articles, appended in the thesis:

I. **Gas chromatographic and mass spectrometric analysis of 36 lignin-related methoxyphenols from uncontrolled combustion of wood.**
Kjällstrand J, Ramnäs O and Petersson G (1998)
Journal of chromatography A **824** 205-210

II. **Methoxyphenols from burning of Scandinavian forest plant materials**
Kjällstrand J, Ramnäs O and Petersson G (2000)
Chemosphere, **41** (5) 7-13 (scheduled)

III. **Phenolic antioxidants in wood smoke**
Kjällstrand J and Petersson G (2000)
Basic manuscript to be complemented with further data

Contents

1. Aim of the study

All over the world, many people are exposed to emissions from small-scale wood burning as well as from forest fires. It is therefore important to establish the chemical composition of smoke from incomplete burning of biomass to investigate environmental and health effects.

During earlier studies at our department, concerning volatile hydrocarbons [Barrefors and Petersson 1995a; Barrefors and Petersson 1995b] and furans [Barrefors *et al.* 1996] in smoke from biomass burning, it was noticed that methoxyphenols constitute a significant part of the organic components of wood smoke. Not only their large proportion but also their potential antioxidant properties aroused our interest. Could these compounds explain why man seems to tolerate wood smoke better than expected with regard to its well-known content of health hazardous compounds?

The aim of this project was to analyse methoxyphenols in smoke from biomass burning. Gas chromatographic retention and mass spectrometric data of specific methoxyphenols were determined to make further studies possible. The second step was to establish identities and relative proportions of methoxyphenols in smoke from burning of different biomass materials. The antioxidant properties of the methoxyphenols were related to chemical structure and to literature data.

2. Burning experiments and analytical methods

With the purpose to simulate the natural course of burning in a furnace for residential heating or a forest fire, wood and other plant materials were incompletely burned in laboratory experiments. The smoke was collected with a gas-tight syringe and analysed with respect to methoxyphenols by gas chromatography and mass spectrometry. The compounds were identified by their mass spectra and gas chromatographic retention times. The combustion efficiency was determined by analysing carbon monoxide and carbon dioxide.

The aim of a first study was to establish analytical data to make further studies possible [**I**, Kjällstrand *et al.* 1998]. In a subsequent study, the methoxyphenol emissions from the burning of wood and other forest plant materials were investigated [**II**, Kjällstrand *et al.* 2000]. A similar but less extensive study was performed for pellets.

2.1 Fuels

Different plant materials were used in the biomass burning experiments. In the first study, season-dried sapwood from spruce and birch were burned [**I**, Kjällstrand *et al.* 1998]. The wood was intended for residential heating. In the second study [**II**, Kjällstrand *et al.* 2000], different plant materials, which were representative for a Swedish boreal forest or clearing, were burned. The plant materials were collected in typical Swedish woodlands, in the surroundings south of the lake Vättern, near the city of Jönköping. They were all characteristic of boreal forest ecosystems.

In the two studies, the materials were divided into smaller parts of the size of a match, and dried at room temperature. The bark and the heather were hard to set on fire. Extra drying in a warming cupboard at 100°C for an hour made it easier.

Several types of biopellets were studied. Pellets made from sawdust were produced at Södra Träpulver in Ulricehamn. Pellets from bark were produced at Södra Skogsenergi AB in Mönsterås. Lignin pellets were obtained from the Swedish Ethanol Development Foundation in Örnsköldsvik, as a by-product from biomass ethanol production.

2.2 Laboratory burning experiments

Our laboratory-scale wood furnace was a ceramic pot. A small pile of about 1g of biomass was ignited and burned in the pot. When the biomass was burning with a flame, the fire was choked by placing another pot upside down over the fire. The drawing in Figure 2.1 illustrates the burning experiment. The upper pot had a bottom hole, through which a smoke sample was collected with a gas-tight glass syringe. Pellets were placed and ignited on a net wire in the fume cupboard, and when burning with a flame, they were placed in the ceramic pot. In the first series of wood burning analyses, the burning experiments were performed outdoors to avoid indoor air contaminants. Later, the pot experiments were performed inside a fume cupboard, which facilitated their performance.

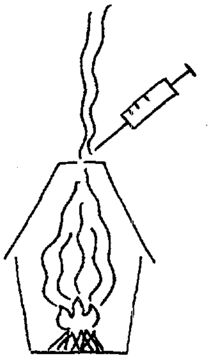


Figure 2.1: Laboratory pot experiment

The reliability of gas syringe sampling was controlled by means of another sampling method, in which a Tenax adsorbent cartridge was used to collect the smoke components. An injector glass liner was filled to one third with Tenax adsorbent material. Smoke was drawn through it using a syringe or a pump. The adsorbed compounds were released onto the column by thermal desorption in the injector of the gas chromatograph.

For the carbon monoxide and carbon dioxide analysis, samples were taken through the bottom hole with a larger gas-tight syringe.

2.3 Identification and quantification

The purpose of the first study was to establish gas chromatographic retention data and mass spectrometric data for the methoxyphenols [**I**, Kjällstrand *et al.* 1998]. In the forest plant material study, concentrations and relative proportions of methoxyphenols were established [**II**, Kjällstrand *et al.* 2000].

The smoke samples were injected into a gas chromatograph coupled to a mass spectrometer. On passing the gas chromatographic column, the smoke components are separated into pure compounds, which are transferred to the mass spectrometer. In the ion source, they decompose to fragment ions by electron impact ionisation. Each compound decomposes in a unique way and the fragment ions give rise to a mass spectrum, which can be regarded as a fingerprint of the compound.

A column with an unpolar methylsilicone stationary phase was used in the first study. The stationary phase used in the later studies consists of a polysiloxane with 14% cyanopropyl-phenyl and 86% methyl groups. It is medium-polar and suitable for a wide range of compounds. Very polar compounds, like anhydrosugars and aldehydes, give rise to broader and more tailing peaks. The upper chromatogram of Figure 2.2 illustrates the separation of compounds in a smoke sample.

The methoxyphenols were identified on the basis of gas chromatographic retention time and mass spectrometric fragmentation pattern. Since methoxyphenols are relatively stable towards fragmentation, the molecular ion is abundant in the mass spectrum, which facilitates identification. The compound identification can be further confirmed using selected ion monitoring (SIM) of, for example, molecular ions (Figure 2.2, the lower chromatogram). The total ion current chromatogram shows the sum of the ion currents across the scan range. Using selected ion monitoring, the mass chromatogram for a single mass or for a sum of selected masses can be studied.

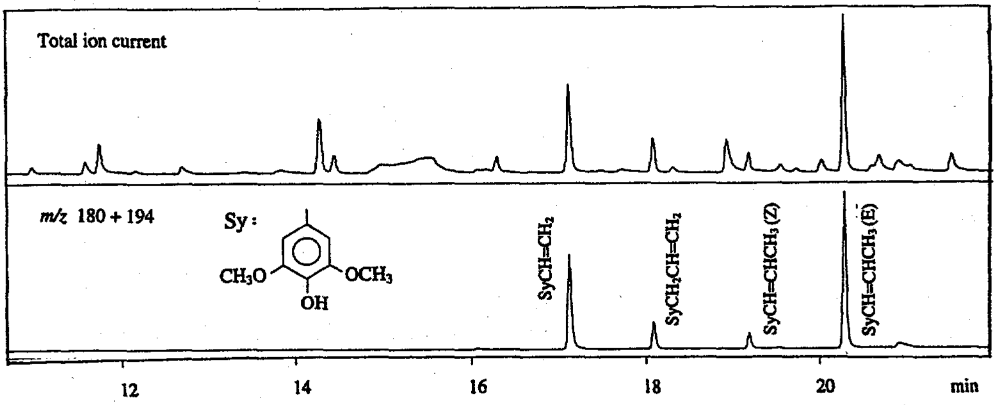


Figure 2.2: Total ion current and selected ion monitoring chromatograms from GC-MS analysis of smoke from birchwood burning [I, Kjällstrand et al. 1998]

Some characteristic ion masses for methoxyphenols are 137 for guaiacyl fragments with a CH_2 group in the sidechain, 167 for the analogous syringyl fragments, 151 for a guaiacyl fragment with an α-carbonyl group and 181 for the corresponding syringyl fragment [**I**, Kjällstrand *et al.* 1998; Meier and Faix 1992]. Gas chromatographic retention times, reference mass spectra [Faix *et al.* 1990a,b] and mass spectral fragmentation path suggestions [Kováčik *et al.* 1969; Kováčik and Škamla 1969; Kováčik *et al.* 1980] for several lignin-derived pyrolysis products are given in the literature.

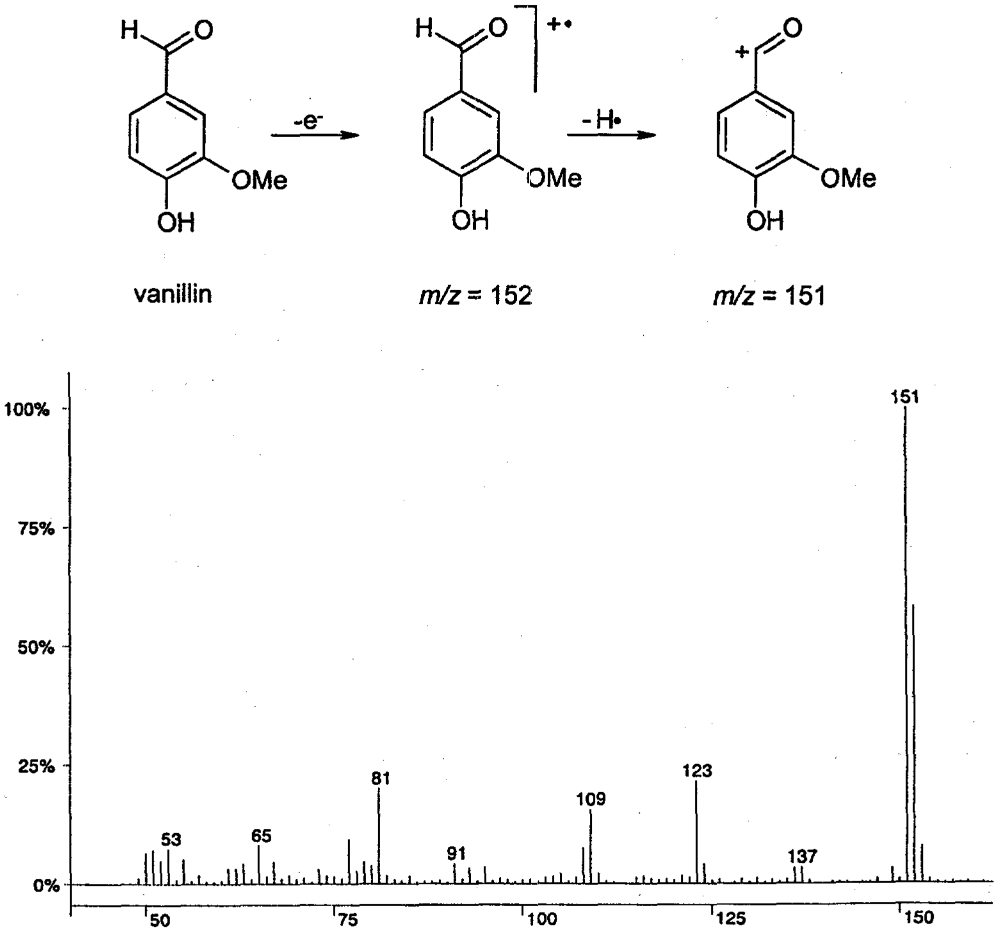


Figure 2.3: Chemical structure, molecular ion, the most important fragment ions and the mass spectrum of vanillin

The methoxyphenol concentrations were determined by use of a reference solution [**II**, Kjällstrand *et al.* 2000]. Vanillin was added to acetonitril in an adequate amount. The response factor was calculated from the peak area of vanillin in relation to the injected amount, and it was used to calculate the concentrations of all methoxyphenols. The correctness of the response factor was confirmed by gas syringe injection of air with a known vanillin concentration.

2.4 Combustion efficiency

The combustion efficiency is defined as the molar emission ratio between carbon dioxide and the sum of carbon dioxide and carbon monoxide, $[CO_2]/([CO_2]+[CO])$. Carbon monoxide and carbon dioxide were analysed using gas solid chromatography with hot wire detection. Smoke samples were collected with a gas-tight glass syringe at the same time as samples were taken for GC-MS analysis of semivolatile organic components. The smoke was injected on a gas chromatograph with two injection valves and two separate columns.

For carbon monoxide analysis, smoke was injected into a molecular sieve column. Molecular sieves are used for separation of compounds with low molecular weights. They consist of inorganic materials with pores of different sizes. For carbon dioxide analysis, smoke was injected into a porous polymer column. The stationary phase was HayeSep Q, a divinylbenzene polymer.

Unfortunately, carbon monoxide and methane elute in the same peak. To determine the contribution from each compound, the methane content was determined using a gas chromatograph with a molecular sieve column and flame ionisation detector. Flame ionisation detectors do not respond to carbon monoxide and carbon dioxide. From this study it was clear that methane constituted only about 10% of the common peak area, and could be neglected in comparison with carbon monoxide.

The combustion efficiency depends on the dry biomass content of the fuels, which was determined according to a standard method (SCAN-C3:78). Plant materials of about 1g were dried to constant weight in a warming cupboard at 105°C and were then cooled down in a desiccator before weighing.

2.5 Combustion sequence

Wood and other biomass materials are heterogeneous and the constituents decompose to release volatiles at different temperatures [Drysdale 1999]. Hemicelluloses decompose in the temperature range 200-260°C, cellulose in the range 240-350°C and lignin not until 280-500°C. The combustion course in a fireplace is commonly divided into four parts. They are described in the table below:

Table 2.1: Fireplace combustion course.

Phase	Temperature	Comments
Drying	100-300°C	Moisture in the fuel is vaporised by heat from the flame and from the walls of the fireplace.
Gasification	300-800°C	After drying, the fuel temperature rises. About 80 % of the fuel is gasified through pyrolysis.
Gas combustion	500-900°C	The volatile gases are blended with air above the fuel bed. Complete combustion is achieved for the right fuel-gas to air ratio at approximately 900°C.
Coal combustion	700-1000°C	The slow combustion of ungasified coal demands sufficient air supply to prevent the coal from leaving the fireplace as dust.

2.6 Comparison with analytical pyrolysis

In analytical pyrolysis, non-volatile compounds are decomposed thermally to volatile compounds in the absence of oxygen [Meier and Faix 1992]. The sample volumes are as small as 1-100μg and should not exceed 50μg to avoid temperature gradients through the samples. The final temperature (typically 500-700°C) is usually reached within 1ms and kept within a narrow range, to obtain optimal thermal fragmentation. The fragmentation products are immediately removed from the heating area to avoid undesired secondary fragmentation reactions.

In a natural fire, the amounts burned are much larger. An oxygen supply is required to maintain a natural fire, but this is usually insufficient to provide complete combustion. Neither in a wild fire nor in a wood furnace is the biofuel homogeneous and completely dried. There are temperature gradients through the materials and the maximal temperature is reached gradually. Secondary reactions occur.

Analytical pyrolysis is a tool for characterising materials through their decomposition products rather than for studying smoke emission. Extensive analytical results have been published for pyrolysis, which are interesting to compare with results from uncontrolled burning. From lignin pyrolysis, methoxyphenols are created with none, one or two carbon atoms in the propanoid sidechain. New double bonds are formed in the sidechains by pyrolytic dehydrogenation. Meier and Faix (1992) have presented the mass spectra of 51 important phenolic lignin pyrolysis products. Large amounts of oxygenated organic compounds have been identified from slow pyrolysis of pine and spruce one-year-twigs [Ingemarsson *et al.* 1998], wood and bark of basket willow [Ingemarsson *et al.* 1999] and of birch twigs [Nilsson *et al.* 1998]. Analytical pyrolysis has also been used to characterise high yield pulps and chemical pulps [Kleen and Gellerstedt 1991]. Bench-scale experiments of smouldering combustion of ponderosa pinewood were performed by McKenzie *et al.* 1994, and their results indicate that the experiments resembled burning rather than pyrolysis.

3. Softwood, hardwood and other plant materials

With the purpose to study methoxyphenols in smoke from a forest fire or a residential wood furnace, different plant materials were burned [II, Kjällstrand *et al.* 2000]. The relative methoxyphenol proportions in the smoke from the burned biomass corresponded well with the lignin structure of different plants. From the methoxyphenol composition in biomass smoke it is possible to tell what kind of plant material that is burning.

The analysis of smoke from burning of different plant materials showed that the main semi-volatile emissions are methoxyphenols and anhydrosugars. The methoxyphenols originate from the decomposition of lignin, while the anhydrosugars originate from cellulose and hemicelluloses. The results agree with the fact that the major structural components in plant biomass are cellulose, hemicellulose and lignin. The lignin structure varies between different plants. This is reflected in our results as differing ratios between syringyl and guaiacyl compounds.

3.1 Lignin in different plants

The lignin content varies between different plants as well as between different parts of the plant and between different morphologic cell layers [Sarkanen and Hergert 1971]. In Table 3.1, concentrations of methoxyphenols and 1,6-anhydroglucose, the main decomposition product of cellulose, in the smoke from burning of different forest plant materials are given.

Conifer wood contains about 30% lignin and deciduous wood 20-25%. Non-woody parts contain only about 10% lignin, which is illustrated in our results. The amount of methoxyphenols relative to 1,6-anhydroglucose is much smaller for needles than for wood. Lignins are only present in vascular plants. On burning of mosses and lichens, no methoxyphenols were obtained.

For the plant, lignin has several essential functions [Sarkanen and Ludwig 1971]. Lignin is important for the internal transport of water, nutrients and metabolites, gives rigidity to the cell walls and acts as a permanent bonding agent between cells in woody parts.

Table 3.1: Concentrations in mg m^{-3} of methoxyphenols and 1,6-anhydroglucose in the smoke from burning of different forest plant materials [**II**, Kjällstrand *et al.* 2000].

	Softwood	Needles	Fern	Grass	Heather	Hardwood
	Pine	*Pine*	*Bracken*	*Wavy hair*	*Calluna*	*Birch*
1,6-Anhydroglucose	**130**	**630**	**150**	**130**	**40**	**60**
2-Methoxyphenols	**150**	**160**	**90**	**190**	**28**	**70**
2,6-Dimethoxyphenols	-	-	-	**80**	**30**	**320**

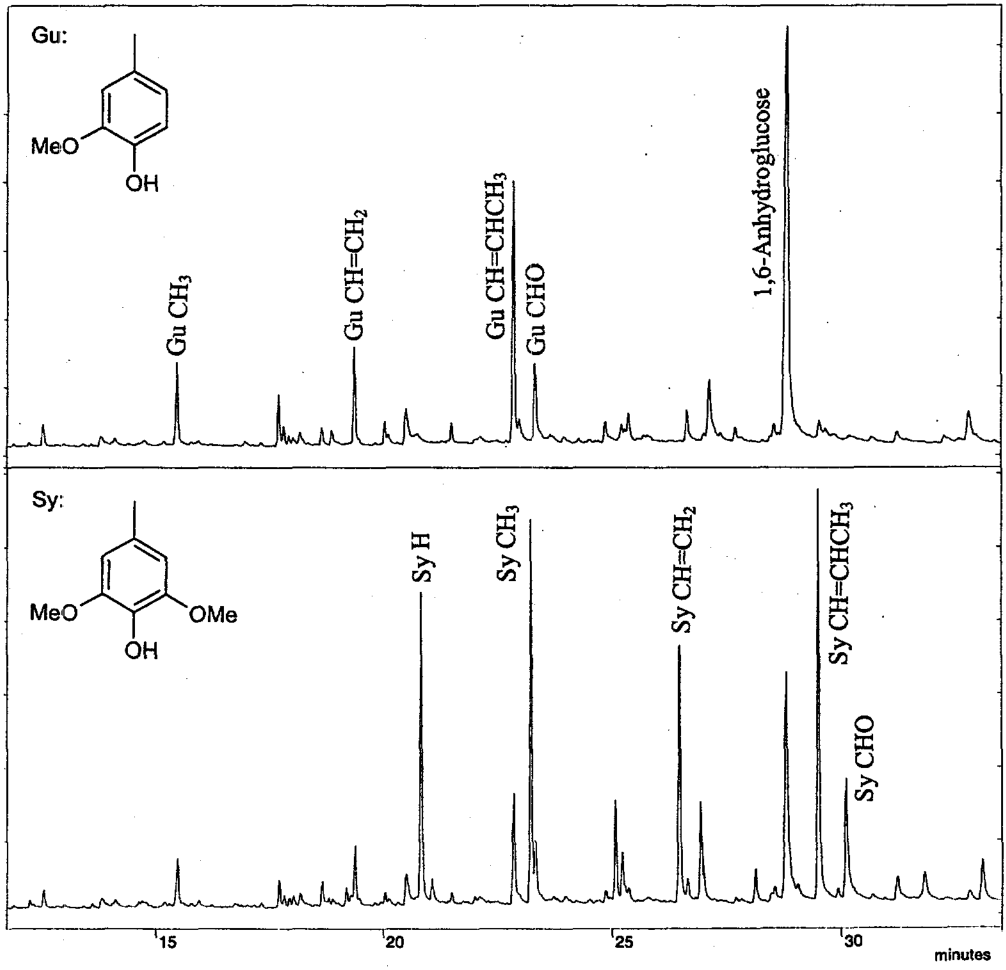


Figure 3.1: Chromatograms from the burning of softwood (spruce) and hardwood (birch), analytical conditions according to II, Kjällstrand et al. 2000

3.2 Methoxyphenol distribution in smoke from biomass burning

Our study of smoke from incomplete burning of different forest plant materials reflects the lignin structure of different plants [**II**, Kjällstrand *et al.* 2000]. We identified 2-methoxyphenols only in smoke from burning of conifer materials and fern (Table 3.1). This corresponds well with the fact that the softwood and fern lignins are built up almost entirely from 2-methoxyphenols. Birchwood smoke contains a large proportion of 2,6-dimethoxyphenols, reflecting the structure of birch lignin. Grass and heather are intermediate with respect to methoxyphenol proportions and lignin structure.

The differences between lignins from different plants are illustrated in Figure 3.1 by the chromatograms. The upper chromatogram originates from an analysis of softwood smoke from the burning of spruce. Most methoxyphenols elute in the range from 15 to 30 minutes and contain only one methoxy group. The main methoxyphenols are methylguaiacol, *trans*-propenylguaiacol and vanillin. The lower chromatogram shows an analysis of hardwood smoke. Most methoxyphenols elute in the range from 15 to 35 minutes and are both 2-methoxyphenols and 2,6-dimethoxyphenols. The main methoxyphenols are syringol, methylsyringol and *trans*-propenylsyringol.

Methoxyphenols are often used as tracer compounds for wood smoke [Hawthorne *et al.* 1988; Hawthorne *et al.* 1989; Sagebiel and Seiber 1993; Simoneit *et al.* 1993].

3.3 The structure of lignins

Lignin is a biopolymer, mainly consisting of the three building blocks guaiacylpropane, syringylpropane and *p*-hydroxyphenylpropane, illustrated in Figure 3.2 [Brunow *et al.* 1999]. Gymnosperm (softwood) lignin mainly contains guaiacylpropane units while angiosperm (hardwood) lignin contains both guaiacylpropane and syringylpropane units. Grass lignin is a copolymer of the three basic units.

As illustrated in Figure 3.3, the lignin structure is irregular and complex. The polymer is branched and cross-linking occurs. There are strong indications of linkages to carbohydrates and some lignins are esterified with phenolic acids. An example is grass lignin, 5-10% of the basic units are esterified with *p*-coumaric acid [Brunow *et al.* 1999]. Several pyrolysis-GC-MS studies have been performed with the purpose to investigate the structure and content of lignin in wood [Faix *et al.* 1990a,b]. In investigations of the maturing and biodegradation processes of plants, methoxyphenols have been identified as pyrolysis products of asparagus [Mellon *et al.* 1994], wheat straw [Rodríguez *et al.* 1997], and of peatified heather from different depths of a raised bog peat deposit [Heijden and Boon 1994].

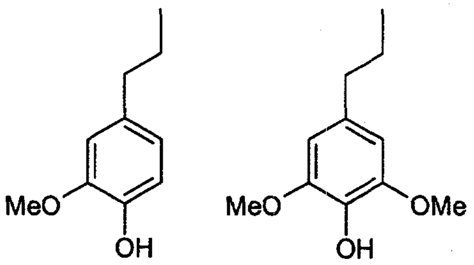


Figure 3.2: The three basic structural units of lignins: guaiacylpropane, syringylpropane and p-hydroxyphenylpropane

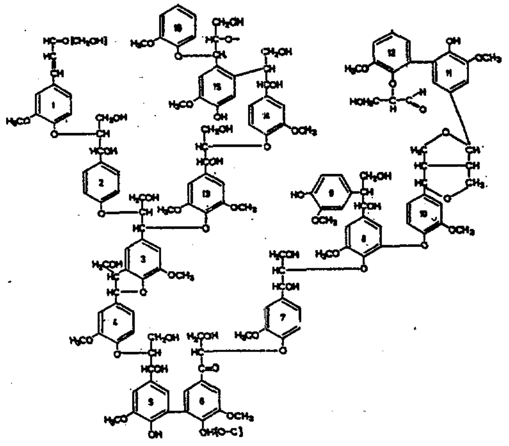


Figure 3.3: Lignin structure proposed by Adler 1977

Lignin is biosynthesised through an enzyme-initiated polymerisation of the three monomers illustrated in Figure 3.4, coniferyl alcohol, sinapyl alcohol and *p*-hydroxycinnamyl alcohol, in varying proportions [Brunow *et al.* 1999].

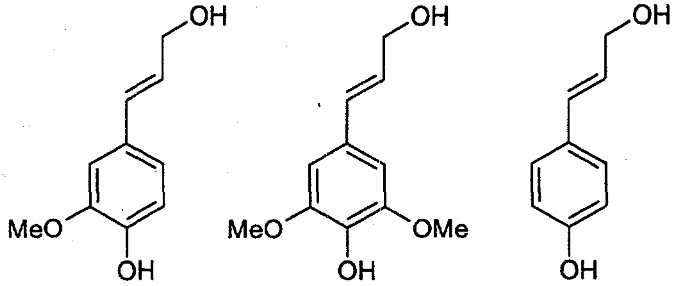


Figure 3.4: Monomers from which the lignin biopolymer is biosynthesised

4. Pellets

During the last few years, the use of biopellets as a fuel for residential heating has increased significantly. This chapter presents basic analytical results for semivolatile compounds in smoke from incomplete combustion of biopellets. Pellets made from sawdust, bark and lignin were incompletely burned in laboratory experiments. The smoke was analysed using gas chromatography coupled with mass spectrometry.

For all three pellet fuels burned, methoxyphenols were predominant among the semi-volatile compounds in the smoke. In the sawdust and lignin pellet smoke, all main semi-volatiles were 2-methoxyphenols (guaiacols). The absence of 2,6-dimethoxyphenols (syringols) reveals that these pellets originated from softwood material only. The smoke from the burning of bark pellets contained both 2-methoxyphenols and 2,6-dimethoxyphenols. Evidently barks from both softwood and hardwood had been used to produce them.

4.1 Pellets in general

The biopellet is a relatively new type of biofuel, produced from biomass waste. It was introduced on the Swedish market during the 1980s and its use has increased significantly since then [Nyström 1995].

The raw materials of the pellets usually consist of sawdust, shavings, bark or chips, which are milled and pressed to small staves of about 8 x 20 mm. A binding agent that increases the strength of the pellet is sometimes added. It may consist of lignin, lignosulphonate or starch [Cronholm *et al.* 1998]. Lignin pellets consist of a washed, pelletised and dried solid lignin residue from the production of ethanol from biomass. The energy content is approximately 30 % higher compared to sawdust pellets.

The biopellet has, as a processed bio fuel, several advantages compared to unprocessed biofuels, like wood [Nyström 1995]. The moisture content is lower and the energy content per weight unit is therefore higher and more uniform. Pellets are also easier to transport and store since their volume is reduced during the milling and pressing operations. Thanks to the improved combustion conditions for pellets, the emissions of air pollutants per produced energy unit tend to decrease.

4.2 Pellet burning experiments

In the present study, three different types of bio pellets (Figure 4.1) were incompletely burned and the semi-volatile compounds in the smoke were analysed. The burned pellets were white pellets produced from sawdust, brown pellets from bark, and lignin pellets. Their dry content was determined to 92.4% for sawdust pellets, 89.4% for bark pellets and 95.5% for lignin pellets by drying at 105 °C to constant weight.

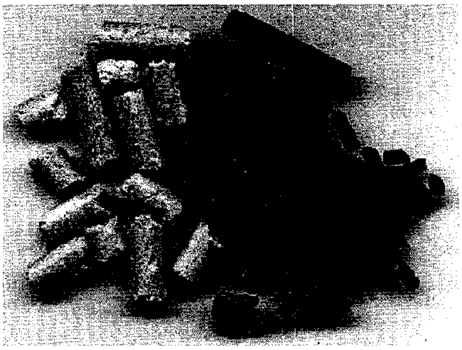


Figure 4.1: Sawdust, bark and lignin pellets (photo: Viveca Larsson)

About 3g of pellets was ignited, using a butane flame, and burned on a wire netting. When approximately half of the material remained, the net with the pellets was placed in a ceramic pot. Another ceramic pot, with a bottom hole, was placed upside down over the fire, to choke the fire. The bottom hole was covered using a piece of glass. When the fire was extinct, a smoke sample was collected through the bottom hole using a 500µl gas-tight syringe. The analytical conditions were the same as those described by Kjällstrand *et al.* 2000.

4.3 Results and discussion

In Figure 4.2, chromatograms from the most representative analyses are presented. Each type of pellets was burned with a subsequent analysis at least tree times, with high reproducibility. In Table 4.1, the percentage proportions and combustion efficiencies for selected methoxyphenols (guaiacyl compounds) are given, and comparisons are made with spruce wood [**II**, Kjällstrand *et al.* 2000]. From Figure 4.2, it is obvious that methoxyphenols are predominant among the semi-volatile compounds in smoke from pellet burning. There are also some anhydrosugars and furan derivatives present among them. The chromatograms in Figure 4.2 cover the retention interval where the quantitatively most important guaiacyl methoxyphenols elute. The earliest eluting syringyl compounds appear in the chromatogram of the bark pellets.

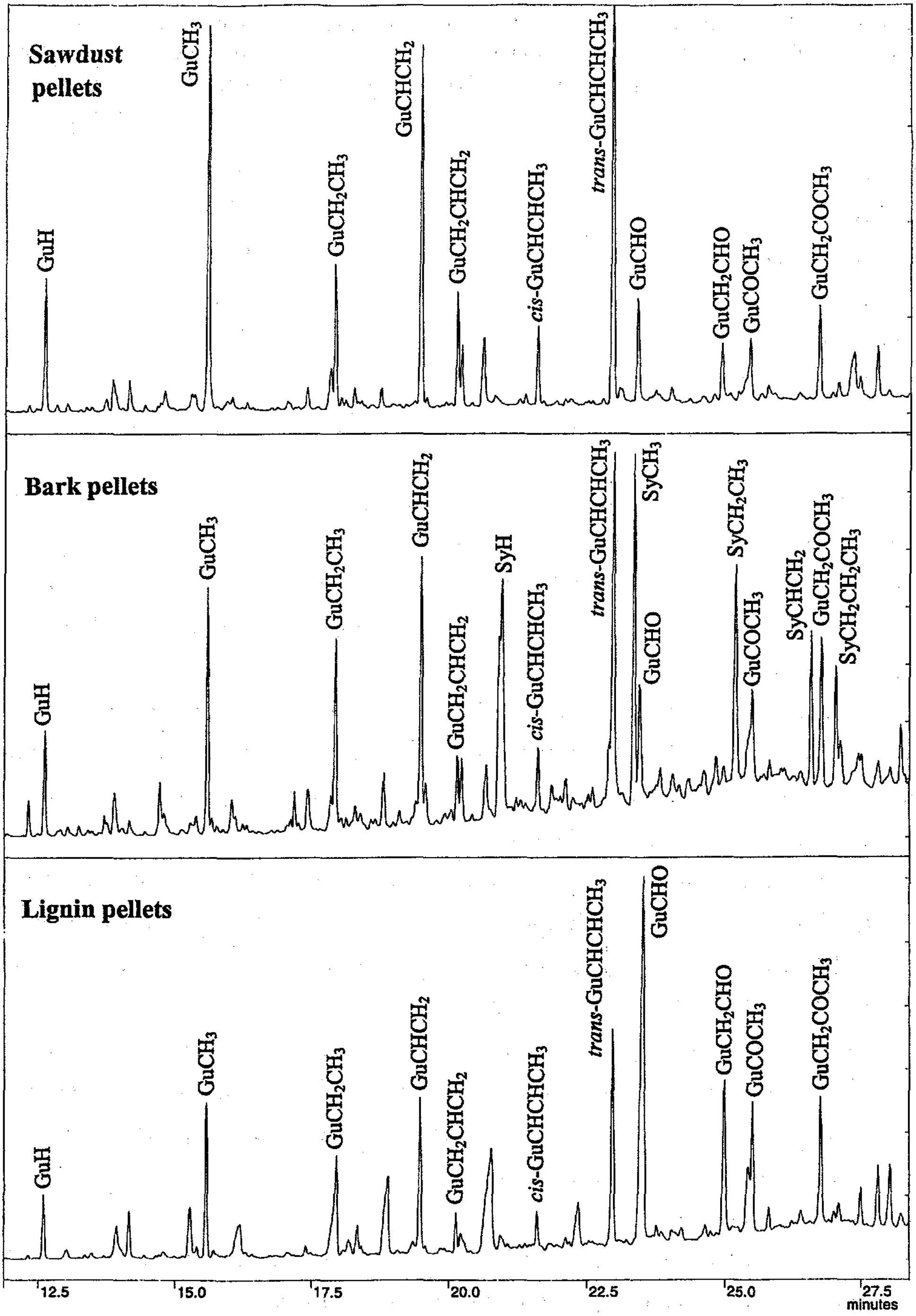


Figure 4.2: Chromatograms (total ion current) from GC-MS analysis of methoxyphenols in smoke from burning of sawdust pellets, bark pellets and lignin pellets (Analytical conditions according to II, Kjällstrand et al. 2000)

Table 4.1: Proportions (% weight of total 4-hydroxy-3-methoxyphenyl, Gu, compounds) of selected methoxyphenols in smoke from biomass burning. Combustion efficiency of the fuels.

	Sawdust pellets	Bark pellets [b]	Lignin pellets	Spruce wood [a]
GuH	5	4	3	4
$GuCH_3$	15	9	7	12
$GuCHCH_2$	14	12	7	9
$GuCHCHCH_3$ (*E*)	20	18	10	19
GuCHO	5	7	26	18
$GuCH_2COCH_3$	4	8	6	6
Combustion efficiency [c]	98	95	93	91

[a] [II, Kjällstrand *et al.* 2000], [b] Proportions for guaiacyl compounds only, [c] CO_2 / (CO_2+CO) %

In the smoke from sawdust pellets and lignin pellets, all main semi-volatiles were 2-methoxyphenols (guaiacols). The absence of 2,6-dimethoxyphenols (syringols) indicates that these pellets originated from softwood material only. In the smoke from sawdust pellets, the methoxyphenols with an alkyl or alkenyl group, particularly propenylguaiacol, were the most prominent.

The smoke from the burning of bark pellets contained both 2-methoxyphenols and 2,6-dimethoxyphenols, indicating that material from both softwood and hardwood had been used to produce them. The quantitatively most important compounds were syringol, methylsyringol, and *trans*-propenylguaiacol.

Lignin pellets almost exclusively contain lignin. This was reflected in the smoke, where components originating from cellulose, i.e. anhydrosugars and furans, were almost absent. Vanillin, 4-hydroxy-3-methoxy-benzaldehyde, was the most prominent compound in the lignin pellet smoke, which actually smelled of vanillin.

The methoxyphenol proportions from spruce wood burning correspond well with proportions for sawdust and bark pellets, except for the proportion of vanillin. Compared to spruce wood, the vanillin content is much lower for sawdust and bark pellets. It should be observed that the different burning characteristics of the wood chips probably influence the methoxyphenol proportions.

The combustion efficiency varied from 90 to 98% between different samples, with the lowest values obtained for bark pellets and the highest for sawdust pellets.

5. Biomass smoke components

The methoxyphenols, formed from lignin, constitute a large part of smoke from incomplete combustion of biomass. The cellulose and the hemicelluloses mainly decompose to anhydrosugars, which constitute another large part. Biomass smoke also contains smaller amounts of hazardous organic compounds. Two often mentioned groups are volatile hydrocarbons and polycyclic aromatic compounds (PAC). Inorganic compounds, formed from all kinds of combustion of carbon-containing fuels, are carbon oxides and nitrogen oxides.

5.1 Methoxyphenols

Together with anhydrosugars, methoxyphenols constitute the most prominent semi-volatile compounds of wood smoke. Dry wood contains about 30 per cent lignin, and the organic fraction of smoke from incompletely burned wood contains a similar proportion of methoxyphenols. Green parts of the plants, such as leaves, grass and needles, contain less lignin. Consequently, their smoke contains a smaller proportion of methoxyphenols. This is reflected in the results from burning of different forest plant materials [**II**, Kjällstrand *et al.* 2000]. The chromatogram in Figure 5.1 illustrates the predominance of methoxyphenols in birchwood smoke.

5.2 Anhydrosugars and furan derivatives

In addition to lignin, the main components of wood are cellulose and hemicelluloses. They decompose primarily to anhydrosugars on heating, but also to furans. Like the methoxyphenols, anhydrosugars and furans are characteristic of smoke from biomass burning. Polysaccharide degradation products from analytical pyrolysis of wood have been studied [Faix *et al.* 1991a,b]. Gas chromatographic retention times, mass spectral data, mass spectra and structural formulas were presented. The hemicelullose fractions of beech wood have been studied by pyrolysis-gas chromatography-mass spectrometry [Pouwels *et al.* 1987].

The most prominent anhydrosugar in smoke from inefficient burning is levoglucosan, 1,6-anhydroglucopyranose [Kleen and Gellerstedt 1991; **II**, Kjällstrand *et al.* 2000]. It originates mainly from cellulose [Pouwels *et al.* 1987] and is emitted in such high concentrations that it can be detected at considerable distances from the original combustion source [Simoneit *et al.* 1998]. The chromatogram in Figure 5.1 illustrates the significance of levoglucosan in smoke from birchwood burning.

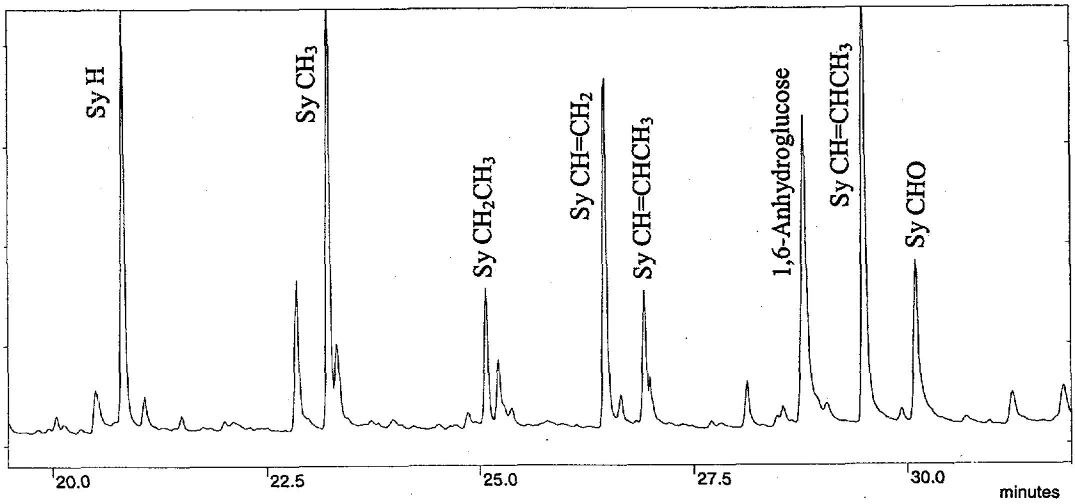


Figure 5.1: Chromatogram of smoke from birchwood burning (Analytical conditions according to II, Kjällstrand et al. 2000). All significant peaks in this retention interval except levoglucosan are methoxyphenols. The most prominent are 4-hydroxy-3,5-dimethoxyphenyl, syringyl (Sy), compounds.

Furans are formed from the decomposition of wood polysaccharides, especially during the glowing and smouldering burning of wood. The content of furans in the smoke decreases with increasing combustion efficiency. Several furans can be seen in methoxyphenol analyses although they elute earlier than methoxyphenols on gas chromatographic columns.

Furfural (2-furancarboxaldehyde) and hydroxymethylfurfural (Figure 5.2) are characteristic components in smoke from biomass burning. Furfural, which is a thermal decomposition product of xylan hemicelluloses, is a prominent furan derivative in wood smoke [Edye and Richards 1991; McKenize *et al.* 1995; Rodríguez et al. 1997; Pérez-Coello *et al.* 1998]. The furfural concentration decreases rapidly with increasing combustion efficiency.

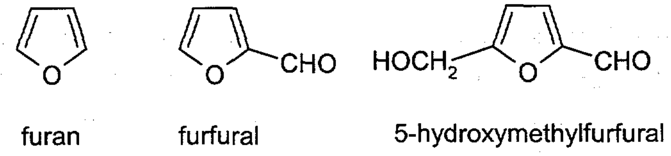


Figure 5.2: Characteristic furans in smoke from biomass burning

Furan and several alkyl furans were previously identified in birchwood smoke [Barrefors *et al.* 1996]. The most prominent were furan and 2-methylfuran. For glowing combustion, the amount of volatile furans was almost as high as the amount of volatile hydrocarbons, but for flaming combustion the corresponding proportion of furans was only a few per cent.

5.3 Volatile hydrocarbons

Although volatile hydrocarbons in wood smoke have received a great deal of attention, they constitute less than ten per cent of the smoke from inefficient burning of wood. The carcinogens benzene and 1,3-butadiene are particularly health hazardous. However, the most important source of benzene in urban air is vehicle emissions.

The relative proportions of a large number of volatile hydrocarbons (C_2-C_8) have been determined for biomass smoke [Barrefors and Petersson 1995a]. The concentrations of volatile hydrocarbons decreased considerably for efficient flaming combustion of wood, and the proportions changed towards ethyne, ethene and benzene [Barrefors and Petersson 1995b].

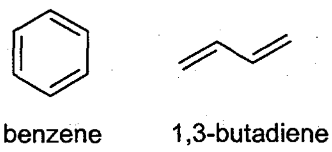


Figure 5.3: Benzene and 1,3-butadiene are two health hazardous, quantitatively important, volatile hydrocarbons in smoke from biomass burning.

5.4 Polycyclic aromatic compounds

The burning of biomass as well as petroleum fuels gives rise to various polycyclic aromatic compounds (PAC). These compounds are formed in small amounts but many of them are highly toxic. They are fat-soluble compounds containing at least two aromatic rings. Polycyclic aromatic compounds are semi-volatile and particle-bound like the methoxyphenols. Although not volatile, they can spread over large areas, since they are transported adsorbed on small particles.

Polycyclic aromatic hydrocarbons (PAH) are well known from diesel exhaust but are also present in wood smoke. Many PAHs are carcinogenic and some of them belong to the best known carcinogenic compounds. Nitrogen containing PACs are more difficult to analyse, but can be even more health hazardous.

Vehicle exhaust appears to be a more significant source of PAH than wood smoke in winter urban air [Hawthorne *et al.* 1992]. Compared to the burning of pine and oak wood, the emission rates of PAH are larger for the burning of synthetic logs, made from petroleum products and sawdust [Rogge *et al.* 1998]. The concentrations of PAH and syringaldehyde in outdoor air were investigated in a small German town, where residential wood combustion was used for heating during the winter [Marbach and Baumbach, 1998]. Both PAH and syringaldehyde concentrations were found to increase with decreasing outdoor temperature. The PAH levels in smoke from natural untreated wood burning and corresponding chimney soot were determined [Launhardt *et al.* 1998]. The highest levels were obtained for a stove with old technology and for wood with a high water content.

5.5 Other organic biomass smoke components

Several types of biogenic compounds are released unchanged into smoke on heating. Terpenes are emitted from incomplete burning, as well as from storing of conifer wood. Pinewood mainly emits the monoterpenes α-pinene and 3-carene, while the most prominent monoterpenes from spruce wood are α-pinene and β-pinene [Strömvall and Petersson 1991]. Lignans are basically dimers of *p*-coumaryl, coniferyl and sinapyl alcohols and believed to serve the plants as toxins. They are significant components of pinewood smoke, but less prominent in oak wood smoke [Simoneit *et al.* 1993, Rogge *et al.* 1998]. Resin acids are synthesised mainly by conifers and are released during the combustion of conifer wood [Rogge *et al.* 1998].

Wood and other biomass contain higher proportions of oxygen than most other fuels. Wood smoke therefore contains high proportions of degradation products with a high oxygen content. Acetic acid is the dominant volatile acid in wood smoke from smouldering burning and often the most abundant condensible compound [Edye and Richards 1991; McKenzie *et al.* 1994; McKenzie *et al.* 1995]. Other major condensible products are methanol, acetol and vinyl acetate. Aldehydes such as formaldehyde and acrolein are formed in significant amounts [Larsen *et al.* 1992; Nilsson *et al.* 1999]. They are believed to cause cancer and allergy.

Among many types of toxic trace components are the well-known dioxins and nitrosamines. Smoke from pure biomass burning is not a great source of dioxins (polychlorinated dibenzo-*p*-dioxins and dibenzofurans), but contaminated biofuels may cause increased dioxin emissions. The dioxin formation increases somewhat when bark-containing fuels are burned [Andersson and Marklund 1998]. Incineration of paper, cartons, painted wood and wood with PVC gives rise to elevated dioxin concentrations [Launhardt *et al.* 1998]. Wood has much lower nitrogen content than green parts of plants. An investigation of volatile *N*-nitrosamines in combustion smoke of various materials showed that cigarette smoke contains five to ten times more *N*-nitrosamines than wood smoke [Kataoka *et al.* 1997]. Among nine tested heterocyclic amines usually formed during heating of protein-containing food, only one was identified in wood smoke [Kataoka *et al.* 1998].

5.6 Emissions to air of inorganic compounds from biomass burning

The quantitatively most important emissions from biomass burning are carbon dioxide and water. Carbon dioxide is an important greenhouse gas whose concentrations have increased alarmingly during the last century. Although biomass burning produces carbon dioxide, the greenhouse gas contribution is regarded as negligible. Biomass materials are renewable fuels, originating from plants, which have consumed carbon dioxide during their life times.

The well-known carbon monoxide emissions from wood burning indicate an insufficient oxygen supply, leading to incomplete combustion [Hubbard 1997].

In smoke from efficient biomass burning in large-scale plants, emissions of organic compounds are almost negligible. Increased formation of nitrogen oxides at high temperatures is then of great environmental importance. These emissions are usually decreased using different kinds of cleaning technology.

Nitrous oxide, N_2O, is a greenhouse gas and contributes to the stratospheric ozone destruction. Biomass burning may contribute to about seven per cent of atmospheric N_2O [Cofer III *et al.* 1991].

5.7 Aspects on residential biomass burning

A fireplace often improves the indoor air since it supplies natural ventilation. The flame consumes large quantities of oxygen and air. The air in the room with a burning fireplace is consumed and exchanged continuously. Dust and pollutants are sucked into the flame, where they decompose.

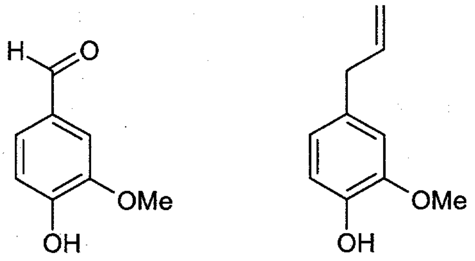
Although there are many advantages with small-scale wood burning, the smoke, however, can disturb the neighbours. Investigations indicate that wood smoke odour annoys about one third of the inhabitants in wood-heated districts [Forsberg *et al.* 1993]. Therefore, and for environmental reasons, it is recommended to use dry fuels and modern environmentally approved combustion furnaces. It is possible to reduce the emissions from wood burning considerably by using a catalyst [Carnö *et al.* 1996].

During the last few years, small particles (0.01-1.0μm) have been increasingly identified as health hazards [Camner 1997]. They originate mainly from vehicle exhaust and stationary burning. There are large differences between wood smoke particles and other particulate matter. Wood smoke particles are characterised by methoxyphenols and polysaccharide degradation products. The estimated lifetime risk from hardwood smoke particles is reported to be smaller than from exhaust particles from gasoline vehicles with catalysts [Cupitt *et al.* 1994].

6. Health aspects of wood smoke methoxyphenols

With what do you associate the smell of wood smoke? For some people it may be danger, while others think of campfires or pleasant moments in front of an open fireplace. Many people associate wood smoke with pollution, like traffic emissions, but there are great differences between wood smoke and car exhausts. One is particularly important: wood smoke contains methoxyphenols, which act as antioxidants, and that may explain how primitive man could tolerate campfires in caves. Methoxyphenols make wood smoke less dangerous.

Could it be that these wood smoke components, the methoxyphenols, even have positive health effects? Firstly, the methoxyphenols do not seem to be hazardous. For example, vanillin is a common food and perfume flavour. Eugenol is frequently used in the dental service and as a spice. Both vanillin and eugenol have been widely used for years, and no severe health hazards have been indicated, although, for example, liquid eugenol can cause allergic reactions on contact with skin.



vanillin eugenol

Figure 6.1: Vanillin and eugenol, two well-known and relatively harmless methoxyphenols

Secondly, the methoxyphenols have antioxidative qualities [**III**, Kjällstrand and Petersson 2000; Ogata *et al.* 1997; Barclay *et al.* 1997]. In smoked food, wood smoke antioxidants prevent lipid oxidation (rancidity). We can expect them to do that in our bodies too. From the chemical structures in Figures 6.1 and 6.2 it is obvious that there is a great resemblance between methoxyphenols and well-known phenolic antioxidants like vitamin E (α-tocopherol) and Q10 (ubiquinol) [Niki 1997].

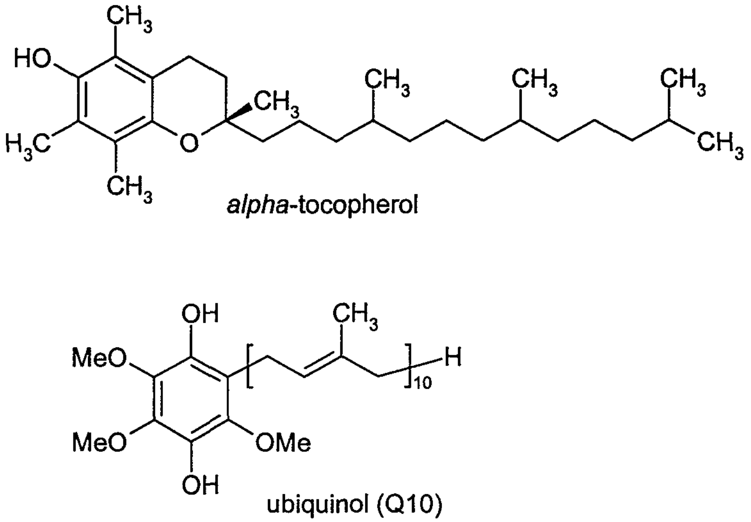


Figure 6.2: Structures of vitamin E (α-tocopherol) and Coenzyme Q (ubiquinol/Q10)

6.1 Free radicals cause diseases

Free radicals have an unpaired electron and are therefore extremely reactive. A free radical attack often leads to a chain reaction, since one or more new radicals are formed. Free radicals can react with cell constituents, for example membrane lipids or DNA molecules [Simic 1992]. Free radical reactions are thought to be one of the main causes of different health illnesses such as asthma, cancer and vascular diseases and to be involved in the ageing process. Cancer can arise from a mutation caused by a free radical injury of the DNA molecule. According to the oxidation theory, arteriosclerosis is initiated by free radical oxidation of components of low-density lipoproteins (LDL) [Upston *et al.* 1999].

Free radicals are continually created in our bodies, since the respiratory chain is leaking free radicals. Well-known radicals are the superoxide radical, $\bullet O_2^-$, the hydroxyl radical, $\bullet OH$, and the hydroperoxide radical, $HOO\bullet$. The formation of radicals increases when hydrocarbons are inhaled, for example from cigarette smoking, car exhausts or wood smoke, since the enzymatic system for hydrocarbon metabolism, with the hemoprotein cytochrome P-450, leaks radicals [Birgerson *et al.* 1995].

6.2 Antioxidants - the cell's defence against free radicals

Several enzymatic systems eliminate metabolically produced oxygen radicals. These enzymes, together with a large variety of antioxidants, constitute an effective defence system. If a free radical nevertheless causes damage to, for example, a DNA molecule, there are sophisticated repair mechanisms in the cells. If they fail, the damage can lead to a mutation causing, for example, cancer.

Antioxidants protect us against free radicals by reacting with them. An antioxidant can provide an electron to a free radical before the free radical attacks important cell structures. A common factor of antioxidants is that they remain fairly stable after reacting with free radicals. Hence they interrupt chain reactions started by free radicals. Antioxidants disarm the free radicals through their own oxidation, a reaction that makes them free radicals themselves - stable free radicals.

Phenolic antioxidants lose a hydrogen atom with an electron from the phenolic hydroxyl group when they are oxidised by a radical. Their remaining unpaired electron on the oxygen atom can be delocalised in the molecule's structure through resonance [Simic 1992]. Thereby the stability of the molecule is increased. In Figure 6.3 the resonance forms of the guaiacol radical are illustrated. Methoxyphenols with a conjugated double bond in the sidechain have even better possibilities to delocalise the unpaired electron. The antioxidant effect is strengthened by methyl or methoxyl groups adjacent to the phenolic hydroxyl group.

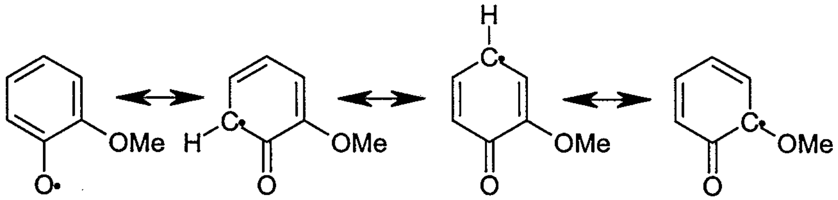


Figure 6.3: The radical of guaiacol is stabilised through resonance.

6.3 Wood smoke antioxidants affect lungs and airways

Interest in antioxidants is normally focused on those obtained from food. They are transported to the cells by the blood after the digestion. Wood smoke and food antioxidants differ with respect to exposure and uptake mechanisms. Since the smoke is inhaled, the antioxidants are rapidly transported to the tissues exposed to particulate air pollutants. Airways and lungs are also exposed to hydrocarbons and oxidising gases like nitrogen dioxide and ozone.

6.4 Differences in antioxidant activity between methoxyphenols

The antioxidant effect of phenols is strengthened by methyl or methoxyl groups adjacent to the phenolic hydroxyl group. Hence, 2,6-dimethoxyphenols in smoke from angiosperm wood burning are more effective antioxidants than 2-methoxyphenols from conifer materials [**III**, Kjällstrand and Petersson 2000]. For efficient inhibition of lipid peroxidation, electron donor or bulky groups at the *ortho* or *para* position of the phenol are required [Ogata *et al.* 1997].

Phenolic compounds with an allyl group on the aromatic ring, such as 4-allyl-2,6-dimethoxyphenol and eugenol, have the ability to scavenge the superoxide ($\bullet O_2^-$) and hydroxyl radicals. Other phenols may play a role in the termination of free radical chain reactions [Ogata *et al.* 1997].

Many studies have established the antioxidative effects of eugenol and isoeugenol [Ogata *et al.* 1997; Priyadarsin *et al.* 1998; Ivanov and Davcheva 1992; Kumaravelu *et al.* 1996; Toda *et al.* 1994]. The antioxidant activity of isoeugenol is twice that of eugenol [Ivanov and Davcheva 1992; Barclay *et al.* 1997]. The higher activity of isoeugenol may be due to the presence of the conjugated double bond, which increases the stability of the phenoxyl radical by electron delocalisation [Rajakumar and Rao 1993].

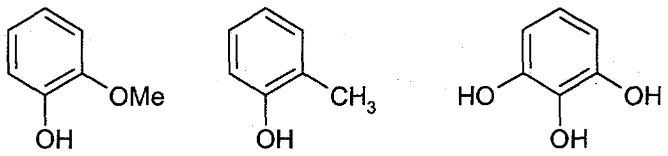
6.5 Wood smoke preserves food

Smoking in food processing, for a better durability and flavour of fish, meat and other foods, is a well-known everyday example of the use of wood smoke antioxidants. It is one of the world's oldest food preservation methods. The food durability is increased by drying the surface and by adding preserving agents from the smoke. If the smoke is warm, the foods are also pasteurised. The quantitatively most important components of the smoke are steam, acetic acid and phenols, but it also consists of volatile and non volatile acids, methanol, formaldehyde, higher aldehydes, ketones and high molecular-weight hydrocarbons [Andersen and Risum 1991].

The primary conserving effect of smoking is said to be the drying of the surface. The smoke content of acids, especially formic and acetic acid, contributes to a pH decrease, leading to a bacteriostatic effect. The formaldehyde content is even more important since formaldehyde is a vigorous disinfection agent. The formaldehyde concentration can reach 1000 mg m^{-3} smoke.

Phenolic antioxidants in the smoke are important for preserving the quality of the food, especially since smoked foods often contain a great deal of fat. The phenols and acids

Phenolic antioxidants in the smoke are important for preserving the quality of the food, especially since smoked foods often contain a great deal of fat. The phenols and acids contribute to the characteristic smoked taste. It is still unclear whether the taste comes from the smoke components, or the products of their reactions with the food.



guaiacol *ortho*-cresol pyrogallol

Figure 6.4: Three phenolic antioxidants in wood smoke.

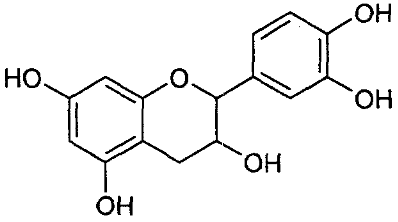
The hardwoods beech, alder and oak are regarded to be the best for food smoking. Juniper and larch woods are also frequently used, since they give a special flavour. Hardwoods should also be preferred since their smoke contains 2,6-dimethoxyphenols, which are stronger antioxidants compared to 2-methoxyphenols. Methoxyphenols and lignin dimers with antioxidant properties have also been detected in liquid smoke flavouring preparations [Guillén and Ibargoitia 1998].

6.6 Dietary antioxidants

The vitamins C (ascorbic acid) and E (α-tocopherol) and certain plant chemicals, such as carotenoids and flavonoids, are antioxidants. Vitamin E is lipophilic and protects cell membranes and other lipid-containing parts of the living cell. The wood smoke methoxyphenols are similar to tocopherols in structure but lack their long lipophilic hydrocarbon chain. Vitamin C works in the hydrophilic parts of the cell and in the blood. Vitamin C, Q10 and glutathione (GSH) can reactivate oxidised vitamin E.

We can increase the antioxidant store of our cells by a well-composed diet. There are plenty of antioxidants in the green parts of plants, to protect them from endogenic and exogenic free radicals. Fruits, seed coats and germs are also rich in antioxidants, needed to protect the new individual. The well-known antioxidant vitamin E occurs in large amounts in fat fish, nuts and vegetable oils. Many plant antioxidants have phenolic structures [Newmark 1996].

During the last few years flavonoids have been much discussed due to their antioxidant activity. They are phenolic antioxidants, which consist of a 15-carbon skeleton compound called flavone (2-phenylbenzopyrone), in which one ore more hydrogen atoms are replaced either by hydroxyl groups or by methoxyl groups. Flavonoids are extensively represented in plants. In tea leafs, flavonoid catechins can constitute up to 30% of the dry leaf weight [Newmark 1996]. Chocolate is an example of a food, rich in the strong phenolic antioxidant catechins [Waterhouse *et al.* 1996; Sanbongi *et al.* 1997; Arts *et al.* 1999].



Epicatechin

Figure 6.5: The flavonoid epicatechin, also called epicatechol, is the quantitatively most important antioxidant in chocolate.

6.7 Synthetic antioxidants

The synthetic antioxidant butyl hydroxytoluene, BHT, is commonly used in foods, cosmetics and other chemical products. It is partially oxidised to a metabolite (Figure 6.6) that has been suspected to cause lung disease. The oxidation occurs in the enzyme system cytochrome P-450 [Birgersson *et al.* 1995]. At least one large alkyl group is required next to the phenolic OH group to cause lung injuries. Another common synthetic antioxidant is BHA, butyl hydroxyanisole.

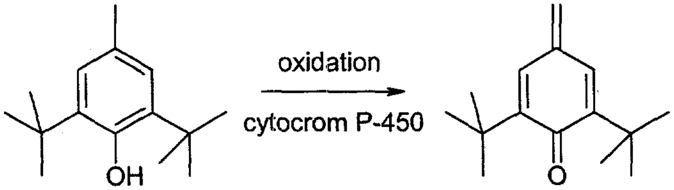


Figure 6.6: Butyl hydroxytoluene is enzymatically oxidised to a harmful metabolite

It has been shown that several methoxyphenols are more effective antioxidants than BHT [Camire 1997, Barclay *et al.* 1997]. According to measurements of peroxidation inhibition rate constants by Barclay *et al.* (1997), the methoxyphenols in Table 6.1 were all more active antioxidants than the synthetic commercial peroxidation inhibitor BHT (2,6-di-*tert*-butyl-4-methylphenol). Compared to the lignin monomers, examined dimeric and tetrameric phenolic lignin model compounds had even higher antioxidant activities.

Table 6.1: Relative antioxidant activity[1] of methoxyphenols and BHT [Barclay *et al.* 1997]

BHT	1.82
4-propylguaiacol	3.07
eugenol	3.33
isoeugenol	7.19
coniferyl alcohol	7.74
coniferylaldehyde	3.58
4-allyl-2,6-dimetoxyphenol	7.45

[1] calculated from the rate of inhibition of styrene peroxidation

6.8 Health hazards from methoxyphenols

Although methoxyphenols can prevent cancer as antioxidants, they can also act as carcinogens under certain circumstances and in certain organs [Asakawa *et al.* 1994; Ito *et al.* 1993]. According to Brusick (1993), phenolic antioxidants are antimutagenic and they do not appear to be mutagens.

One of the most well-known and studied methoxyphenols is eugenol. Liquid eugenol has been found to cause skin allergy on contact. The closely related compound isoeugenol shows even higher allergic activities on skin than eugenol [Chen 1993; Hilton *et al.* 1996]. Maybe they are not the only allergenic methoxyphenols. Neither eugenol nor isoeugenol have a significant potential to cause sensitisation of the respiratory tract [Hilton *et al.* 1996]. Eugenol probably forms a toxic quinone methide metabolite [Thompson *et al.* 1998]. Other methoxyphenols might form similar metabolites.

Only the most fat-soluble methoxyphenols, with large carbon skeletons, tend to accumulate in human tissues [Birgersson *et al.* 1995].

7. Conclusions

- ✓ It is possible to analyse methoxyphenols in smoke from biomass burning with great reliability using gas-syringe or adsorbent sampling and gas chromatography-mass spectrometry. Gas chromatographic retention data and mass spectrometric data are given for 36 methoxyphenols in smoke from incomplete burning of biomass.

- ✓ The methoxyphenols constitute a significant part of the organic fraction of emissions from incomplete biomass burning. They are the dominating semi-volatile compounds followed by anhydrosugars. Total concentrations and relative proportions for specific methoxyphenols in smoke from forest plant materials are given.

- ✓ From the burning of conifer materials, only 2-methoxyphenols are formed, while both 2-methoxyphenols and 2,6-dimethoxyphenols are formed from burning of angiosperm materials. This reflects the lignin structures of different plants. Prominent methoxyphenols in smoke from the burning of pine and spruce wood are 1-propenylguaiacol and vanillin. Prominent methoxyphenols in smoke from the burning of birch wood are 1-methylsyringol and 1-propenylsyringol.

- ✓ Methoxyphenols are antioxidants, which react with free radicals. The resulting methoxyphenol radical is stabilised through resonance. Methoxyphenols with a conjugated double bond in the side chain and with two methoxy groups are more effective antioxidants. The health effect of methoxyphenols in smoke from biomass burning should be further investigated.

8. Acknowledgement

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Supplement:

Physical and chemical properties of methoxyphenols

The methoxyphenols belong to the chemical group phenols, since they have a hydroxyl group attached directly to a benzene ring. They are also ethers, since the oxygen atoms in the methoxy groups are linked to two carbon atoms. The individual methoxyphenols in wood smoke differ in properties due to their different side-groups.

Volatility, boiling points and water solubility

Methoxyphenols are semi-volatile compounds. Although the most volatile methoxyphenols, like guaiacol and methyl guaiacol, appear in the gas phase of wood smoke, most methoxyphenols, especially the 2,6-dimethoxyphenols, have relatively low volatility and are condensed on and constitute particulate matter. Most boiling points are in the range 200-300°C. Guaiacol has its boiling point at 205°C and the well-known compounds eugenol and vanillin have boiling points at 254°C and 285°C respectively.

Phenols have higher boiling points compared to corresponding hydrocarbons with similar molecular mass. Phenol (M: 94.11g mol^{-1}; bp: 182°C) have a 70°C higher boiling point than toluene (M: 92.13g mol^{-1}; bp: 110.6°C). The high boiling points are due to the fact that phenols, like alcohols, have a hydroxyl group forming strong intermolecular hydrogen bonds. They keep the molecules of phenols together and make them less volatile. In contrast to phenols and alcohols, ethers have boiling points that are roughly comparable with those of hydrocarbons of the same molecular mass.

The ability to form strong intermolecular hydrogen bonds makes phenols modestly water-soluble. Eugenol is soluble in alcohol and ether, but difficult to dissolve in water. Ether molecules can not associate with each other like phenols and alcohols, but they are able to form hydrogen bonds to water. Therefore, their water solubilities are similar to those of alcohols of the same molecular mass. The water solubility increases with the polarity of the side-groups. Vanillin is difficult to dissolve in cold water, but dissolves in hot water.

Phenols as acids

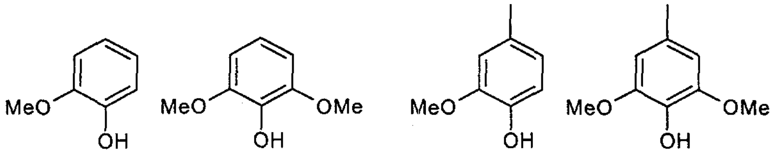
In spite of the structural similarities between phenols and alcohols, the phenols are much stronger acids. Most alcohols have pK$_a$-values in the range 18 whereas the pK$_a$-values of phenols are below 11. The pK$_a$-values of eugenol and isoeugenol are 9.5, [Priyadarsini *et al.* 1998] to be compared with 9.89 for unsubstituted phenol. Phenols are very weak acids compared to carboxylic acids, like acetic acid (pK$_a$: 4.74).

The acidic properties of the phenols are due to delocalisation of the negative electric charge of the phenolate ion in the molecule. Hence the proton is held less strongly. The benzene ring of the phenols acts as an electron-withdrawing group.

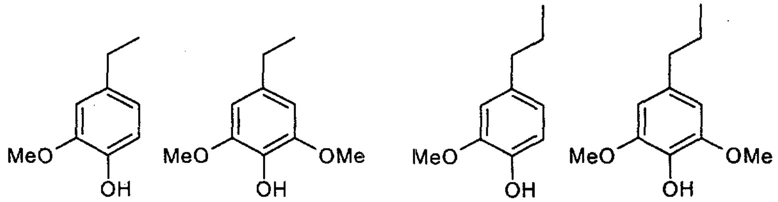
Properties of individual methoxyphenols

The chemical properties of the specific methoxyphenols are to a great extent determined by their sidechain. It can consist of an alkyl group (Figure 1) or an alkenyl group (Figure 2). It can also contain an aldehyde group (Figure 3), a keto group (Figure 4) or an alcohol group (Figure 5). Here, a simplified nomenclature is used, based on guaiacyl (2-methoxyphenyl) and syringyl (2,6-dimethoxyphenyl) units. The side-chain is presupposed to be located in *para*-position to the phenolic hydroxyl group.

Some methoxyphenols are well-known chemicals with wide fields of applications. Guaiacol and methyl-guaiacol (Figure 1) are the main components of medical creosote. It is strongly antiseptic and less toxic compared to phenol. It is used as an inhaler, as an expectorant and as an antiseptic agent for abdomen and intestines.



guaiacol and syringol   methyl-guaiacol and methyl-syringol



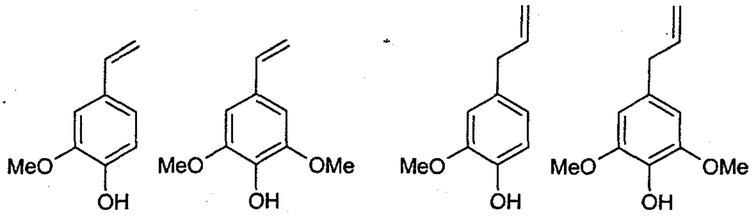
ethyl-guaiacol and ethyl-syringol   propyl-guaiacol and propyl-syringol

Figure 1: Chemical structures of guaiacol, syringol and the alkylated methoxyphenols

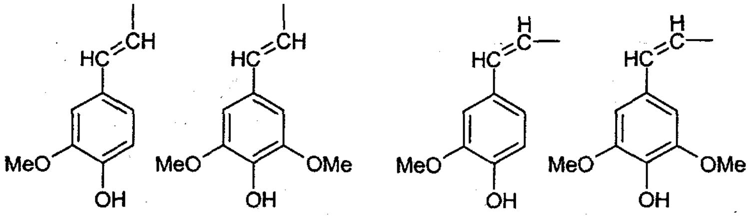
Eugenol (Figure 2) is one of the most well-known and studied methoxyphenols. It is the main constituent of clove oil and occurs also in bayberry and cinnamon oil. Dentists use eugenol in antiseptic bandages and with zinc oxide as temporary filler. Eugenol is strongly antiseptic and is in use as a preservation agent to prevent formation of mould. It has antimicrobial activity [Yang and Chou 1997], is bacteriostatic and fungistatic [Miller *et al.* 1998] and it inhibits the activity of microorganisms [Didry *et al.* 1994]. Liquid eugenol has been found to cause skin allergy on contact.

The closely related compound isoeugenol (Figure 2) shows even higher allergic activities on skin than eugenol, presumably due to its higher convertability to electrophilic structures [Chen, 1993; Hilton *et al.* 1996]. Neither eugenol nor isoeugenol have a significant potential to cause sensitisation of the respiratory tract [Hilton *et al.* 1996].

Eugenol was highly toxic to four species of beetles [Obeng-Ofori and Reichmuth 1997] and to termites [Cornelius *et al.* 1997]. The toxicity may be due to a toxic quinone methide metabolite [Thompson *et al.* 1998].



ethenyl-guaiacol and ethenyl-syringol 2-propenyl-guaiacol and 2-propenyl-syringol (eugenol)



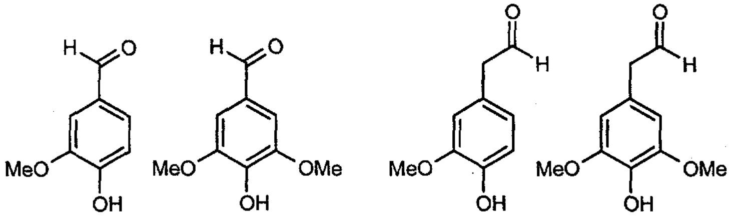
trans-1-propenyl-guaiacol (isoeugenol) and *trans*-1-propenyl-syringol

cis-1-propenyl-guaiacol and *cis*-1-propenyl-syringol

Figure 2: Methoxyphenols with an alkenyl group

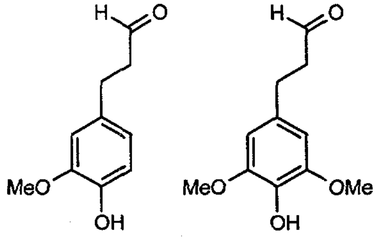
In aldehydes, a carbonyl group is linked to one carbon and one hydrogen atom. Many aldehydes have characteristic odours. The carbonyl group is highly polar. This increases the chemical activities of aldehydes and affects their physical properties. They are easily oxidised to acids and reduced to alcohols. The name aldehyde indicates that they are derived from alcohols by dehydrogenation.

Vanillin (Figure 3) is one of our most important food and perfume flavours. Large amounts are used in the food industry and toiletries production. Vanillin has a strong vanilla odour and a characteristic taste. Vanillin is extremely common in nature and it is the aromatic compound in the vanilla capsule. Vanillin is commercially produced from lignosulfonic acid, a by-product from chemical pulp production.

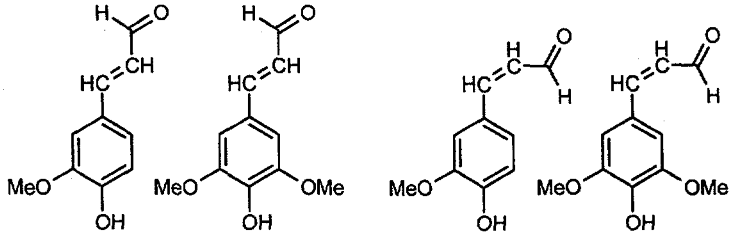


vanillin and syringaldehyde

guaiacylethanal and syringyletanal (homovanillin)



guaiacylpropanal and syringylpropanal

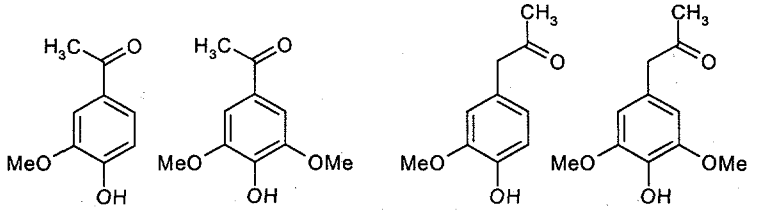


trans-coniferylaldehyde and *trans*-sinapylaldehyde

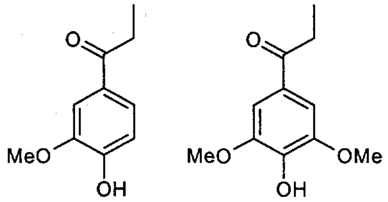
cis-coniferylaldehyde and *cis*-sinapylaldehyde

Figure 3: Methoxyphenols with an aldehyde group in the sidechain

In ketones (Figure 4), a carbonyl group is linked to two carbon atoms. Ketones are highly reactive, although less reactive than aldehydes. The carbon atom in the carbonyl group is susceptible to attack by nucleophiles, since it has a partial positive charge. Typical reactions include reduction and nucleophilic addition. Compared to hydrocarbons, aldehydes and ketones have considerably higher boiling and melting points, due to the polarity of the carbonyl group.

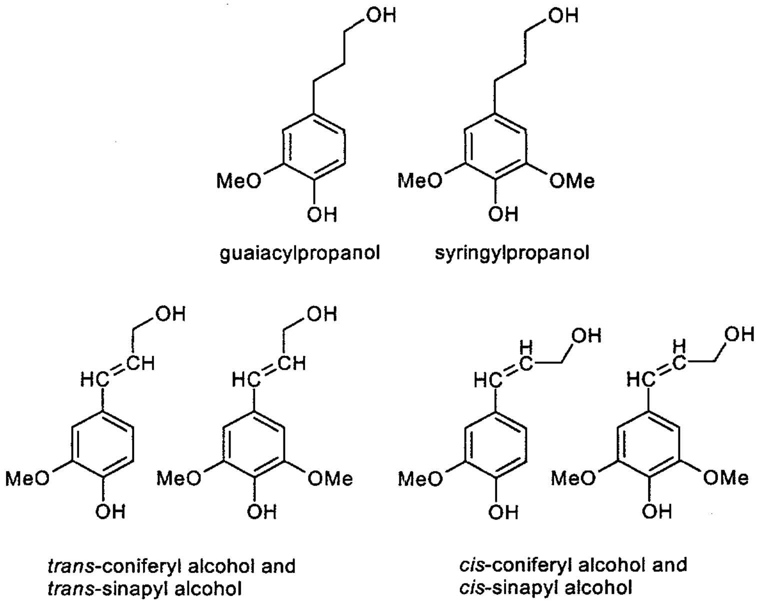


acetyl-guaiacol and acetyl-syringol   acetonyl-guaiacol and acetonyl-syringol



propionyl-guaiacol and propionyl-syringol

Figure 4: Methoxyphenols with a keto group in the sidechain



guaiacylpropanol

syringylpropanol

trans-coniferyl alcohol and
trans-sinapyl alcohol

cis-coniferyl alcohol and
cis-sinapyl alcohol

Figure 5: Methoxyphenols with an alcohol group in the sidechain