

# Phenolic Antioxidants from Lignin Pyrolysis

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# Pyrolysis of Wood and Lignin

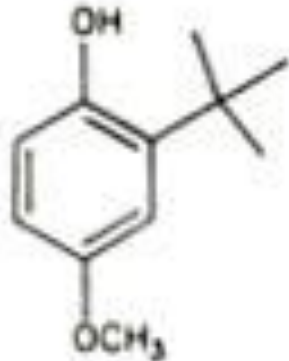
Heating wood particles , birch lignin, or commercial Kraft lignin under nitrogen affords a distillate (bio-oil) that contains a great variety of compounds.



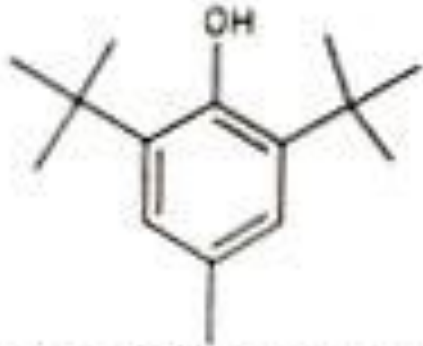
Pyrolysis ( 450 ° C)

Selective extraction of bio-oil gives a fraction that is rich in phenolic compounds.

# Synthetic Antioxidants



butylated hydroxyanisole (BHA)



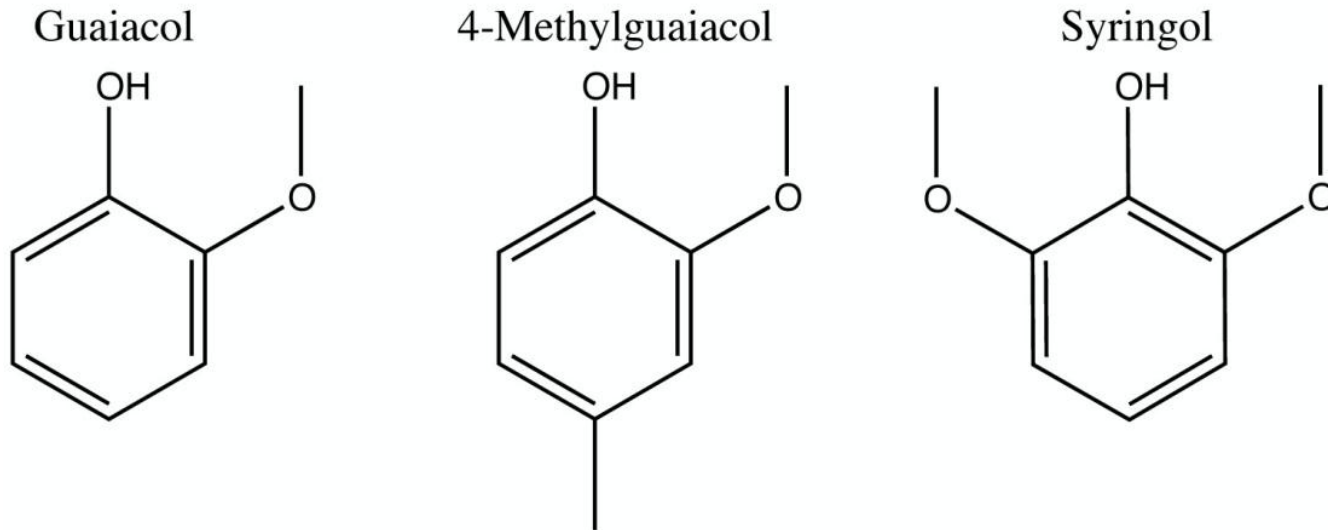
butylated hydroxytoluene (BHT)

BHT production 1.2 million lb (2000):  
BHA 500,000 lb (2006)

Synthesized from petroleum; used in numerous products ranging from breakfast cereal to fuel oil

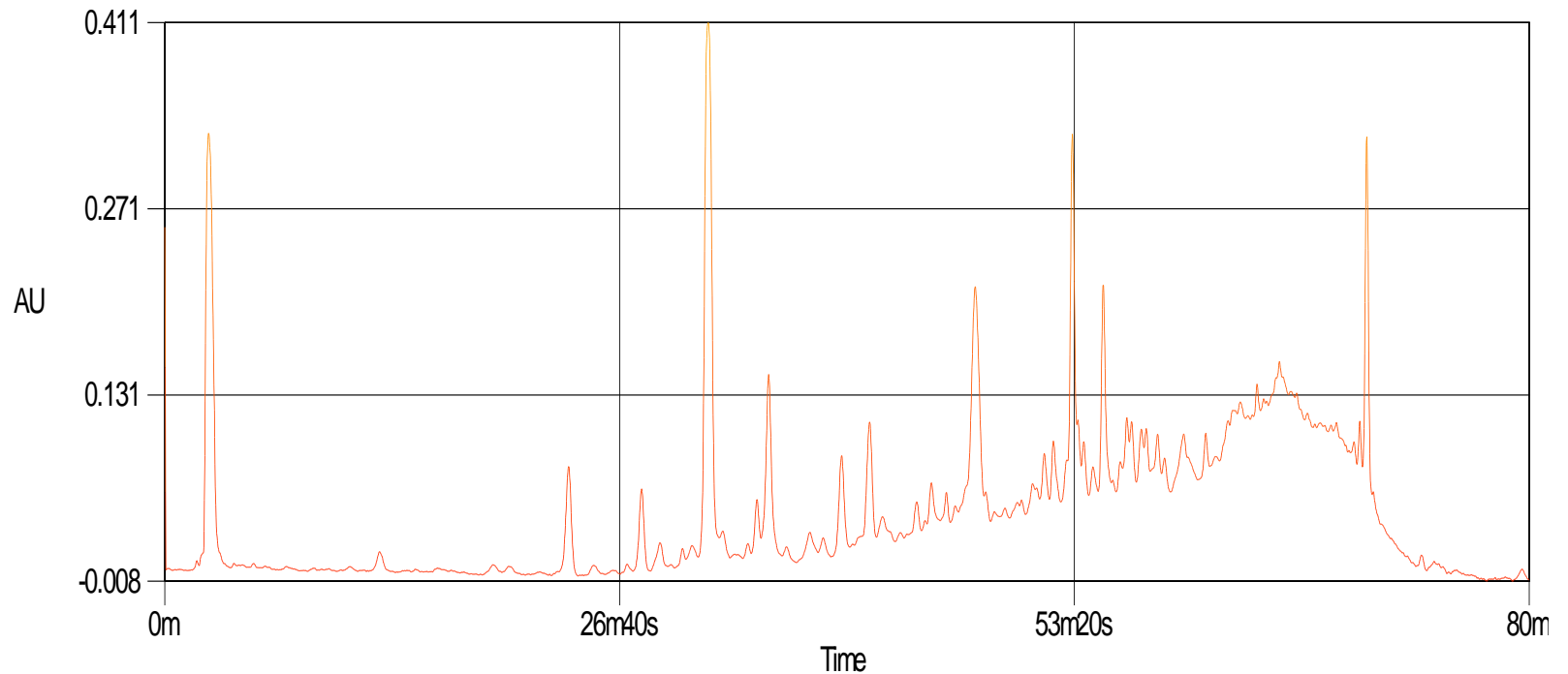
Health effects uncertain

# Potential Natural Antioxidants



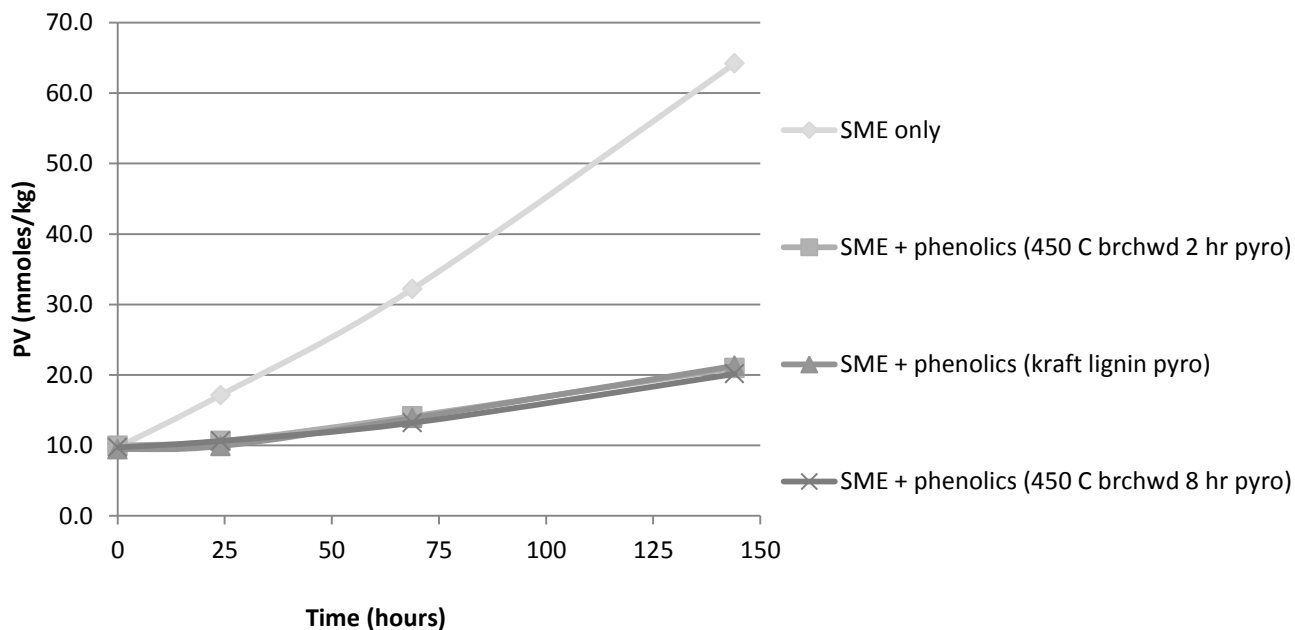
Structurally similar to BHT and BHA; potentially available from lignin, a natural polymer found in plant cells (especially wood)

The phenolic fraction was examined by gas chromatography - mass spectrometry (GC-MS) and by high-performance liquid chromatography (HPLC), revealing a complex mixture of compounds:



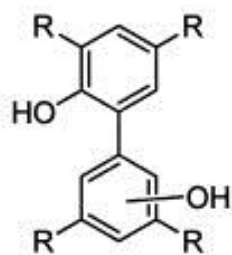
The total phenolic fraction from either hardwood or softwood lignin was effective in an antioxidant assay (Mihalevic et al., 1996) using biodiesel – it was comparable in activity to an equivalent amount of BHT.

### Peroxide formation at 60 C

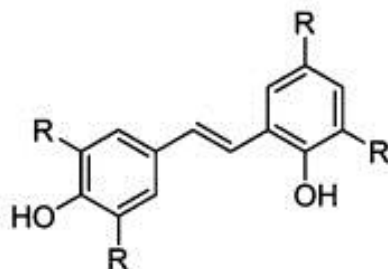


Fraction #	Antioxidant evaluation	Components tentatively identified by hplc
1		
2		
3	no effect	alkylated guaiacols (methyl, ethyl, etc)
4	no effect	phenolic aldehydes, dimers
5	pro-oxidant	phenolic aldehydes, dimers
6	no effect	
7	no effect	phenolic aldehydes
8	anti-oxidant	methylguaiacol, dimers, oligomers? trace amounts of phenolic aldehydes
9	anti-oxidant	dimers? oligomers?
10	anti-oxidant	guaiacol, oligomers?
11		
12		guaiacol, oligomers?
13		
14	anti-oxidant	oligomers?
15	anti-oxidant	oligomers?
16	slight anti-oxidant	oligomers?

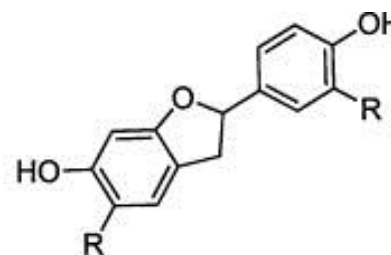
The later-eluting fractions also contain larger molecules, perhaps including dimers or higher oligomers.



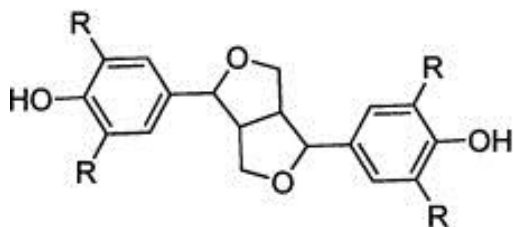
1 Biphenyl



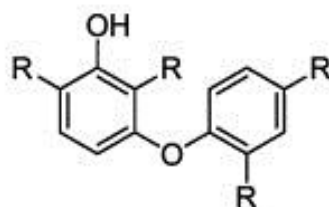
2 Stilben



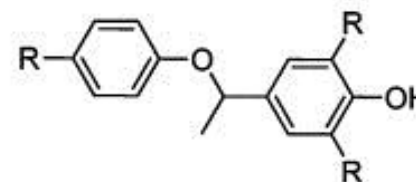
3 Phenycoumaran



4 Resinol



5 Diphenyl ether



6 Alkyl-aryl ether

R = H, OMe, Additional Phenolic Units

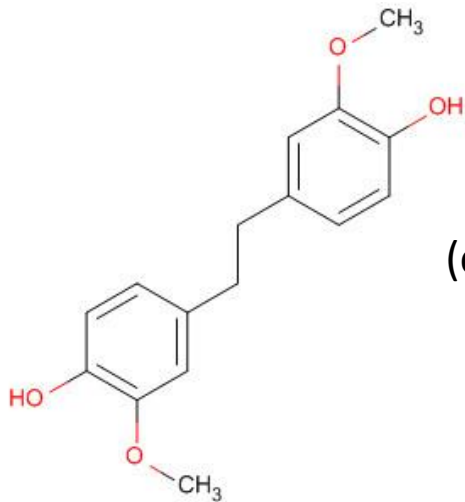
Bayerbach and Meier, J. Anal. Appl. Pyrol. 85:98 (2009)



Possible dimers in our fractions:

Guaiacol mw 124  $\Rightarrow$  Dimer mw 246

4-Methylguaiacol mw 138  $\Rightarrow$  Dimer mw 274 (several)



(one possibility)

The remaining question: what is/are the active antioxidant(s)?