

**FUNDAMENTAL DELIGNIFICATION  
CHEMISTRY OF HIGH- LIGNIN CONTENT  
KRAFT PULPS BY  
LACCASE-MEDIATOR SYSTEMS**

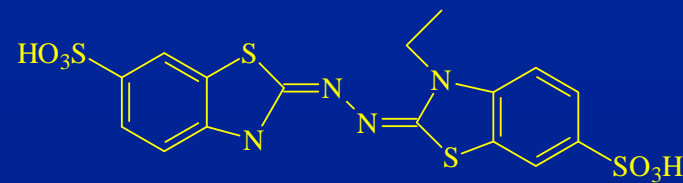


# Mediators-1<sup>st</sup> generation

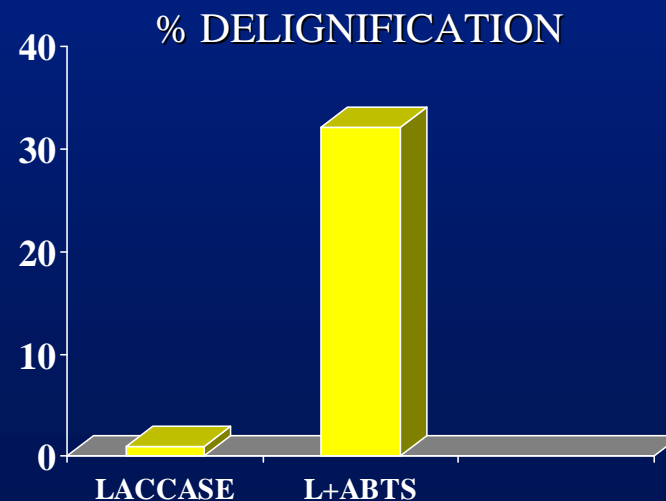
## ABTS:

- 1-First mediator used to demonstrate that a laccase-mediator system can delignify kraft pulps.

**Not ideal >> low delignification levels and cost prohibitive.**

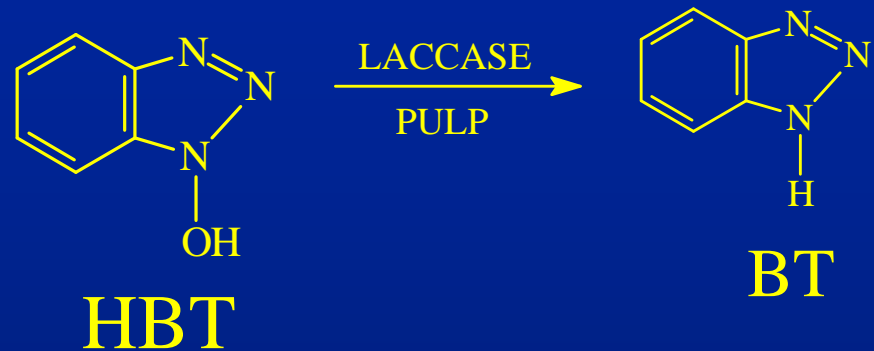


ABTS



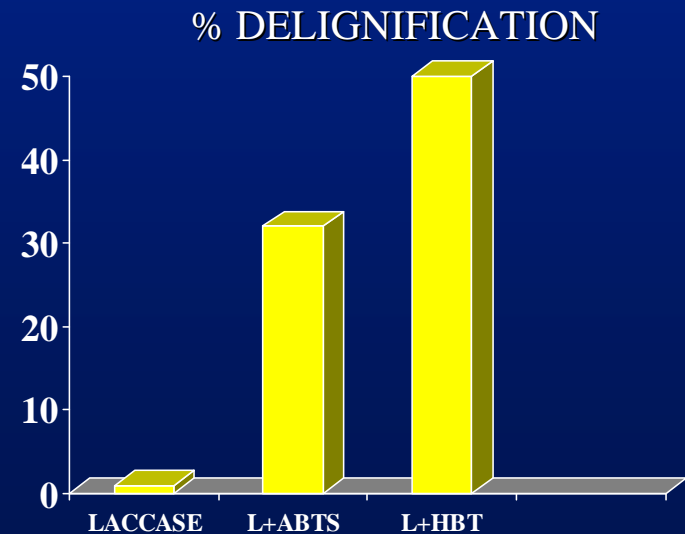
## Mediators-2<sup>nd</sup> generation

- ▲ **HBT**: 1-hydroxybenzotriazole  
(Call, 93)



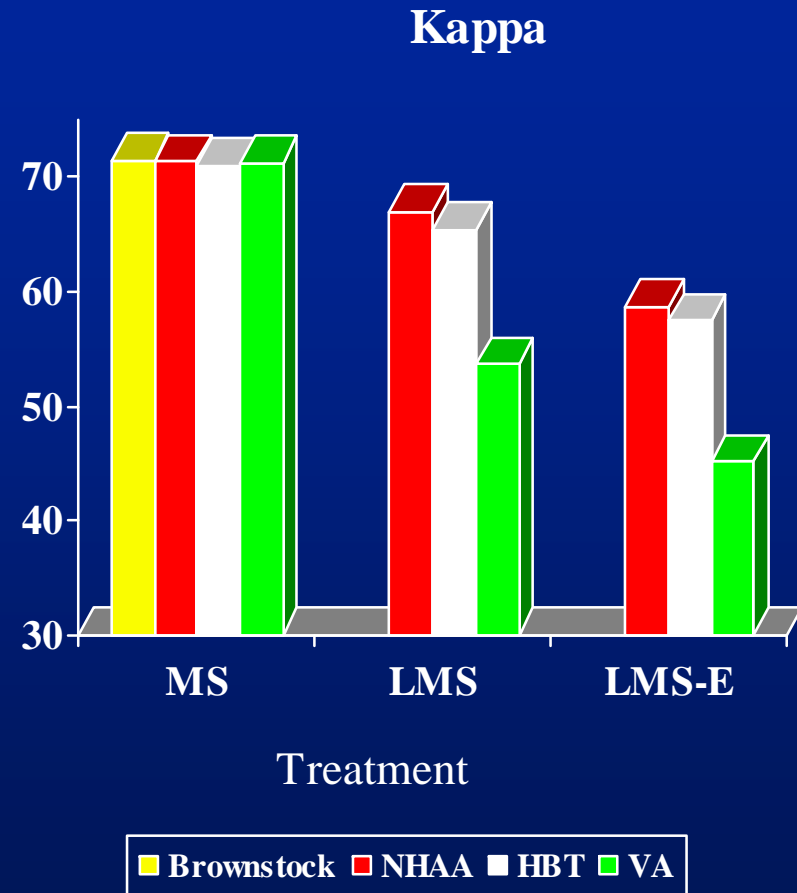
- High delignification levels and selectivity.

Still not ideal >> formation of benzotriazole, interference with the enzyme, and cost prohibitive.



# *Kappa*

- Constant kappa in the absence of laccase.
- VA superior mediator in comparison to HBT and NHAA
- As expected, further drop in kappa after E stage

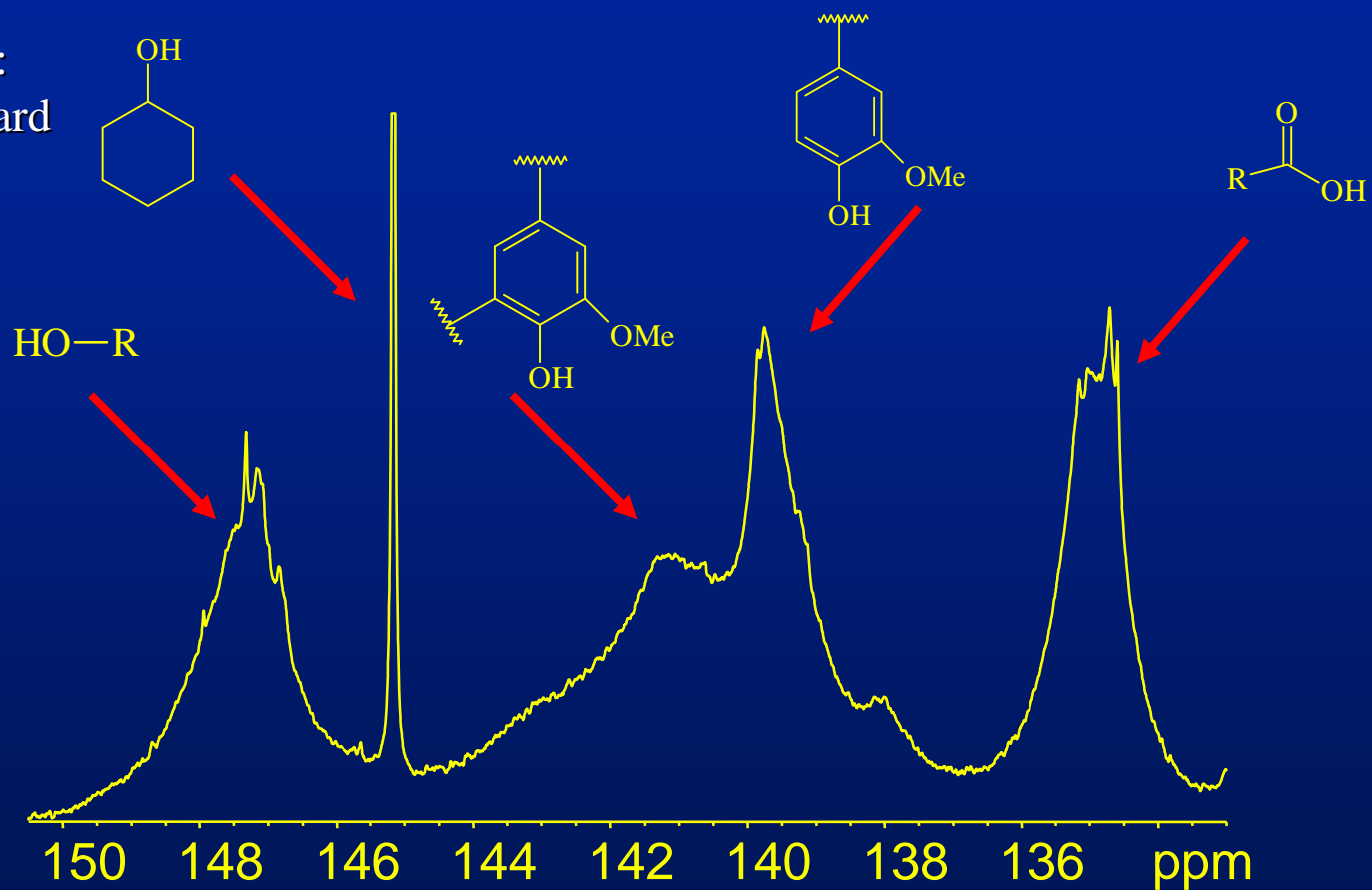


Std. dev. = 0.31

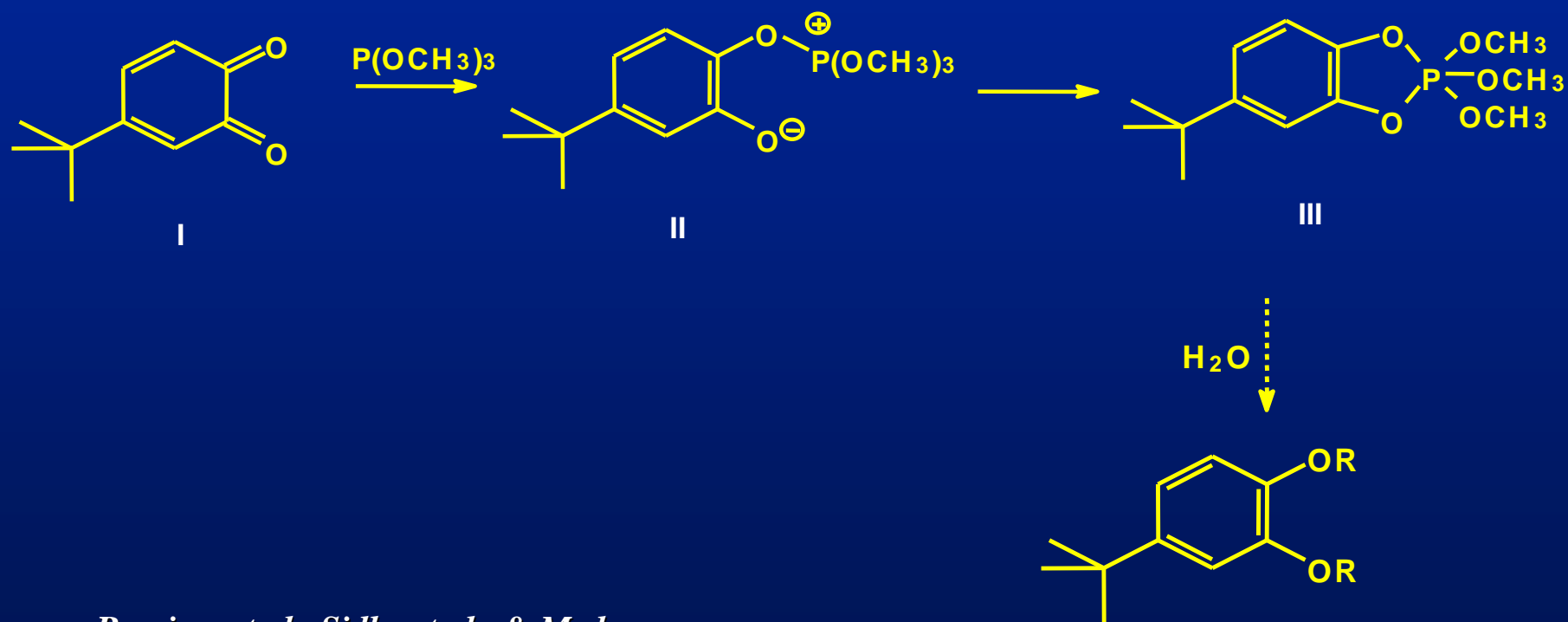


# Typical $^{31}\text{P}$ NMR spectrum

Cyclohexanol:  
Internal standard



# Trimethylphosphite Chemistry: Reaction with Ortho-Quinone Structures

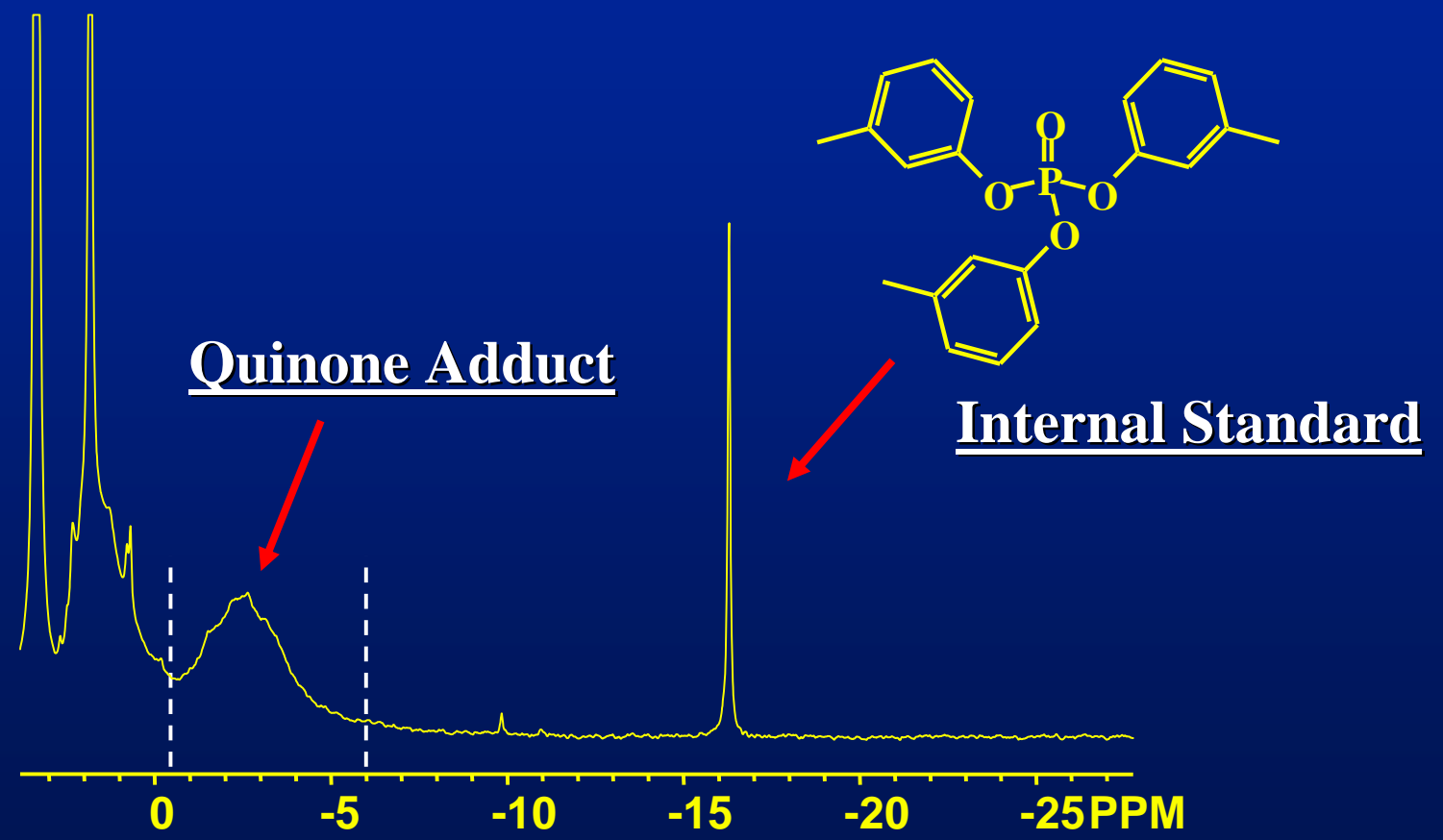


Ramirez et al., Sidky et al., & Medvecz

$\text{R} = \text{PO(OCH}_3\text{)(OH)}$  or  $\text{H}$



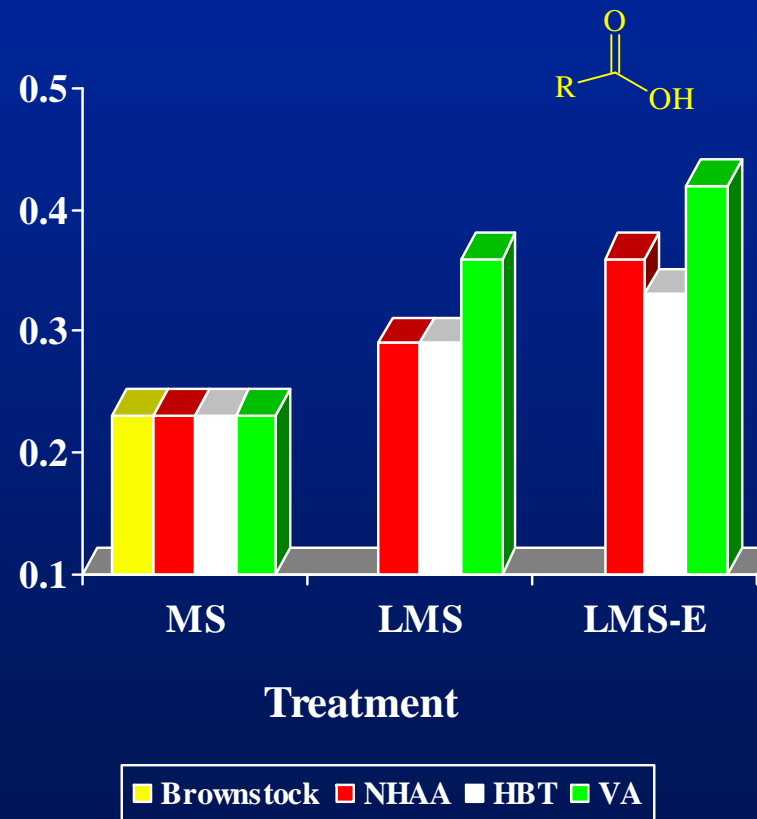
# A typical $^{31}\text{P}$ NMR-TMP Spectrum



# Carboxylic acid groups

- No effect in the absence of laccase
- Increase in carboxyl moieties during LMS: largest with VA
- Enrichment after E stage

Carboxylic acid (mmole/g lignin)

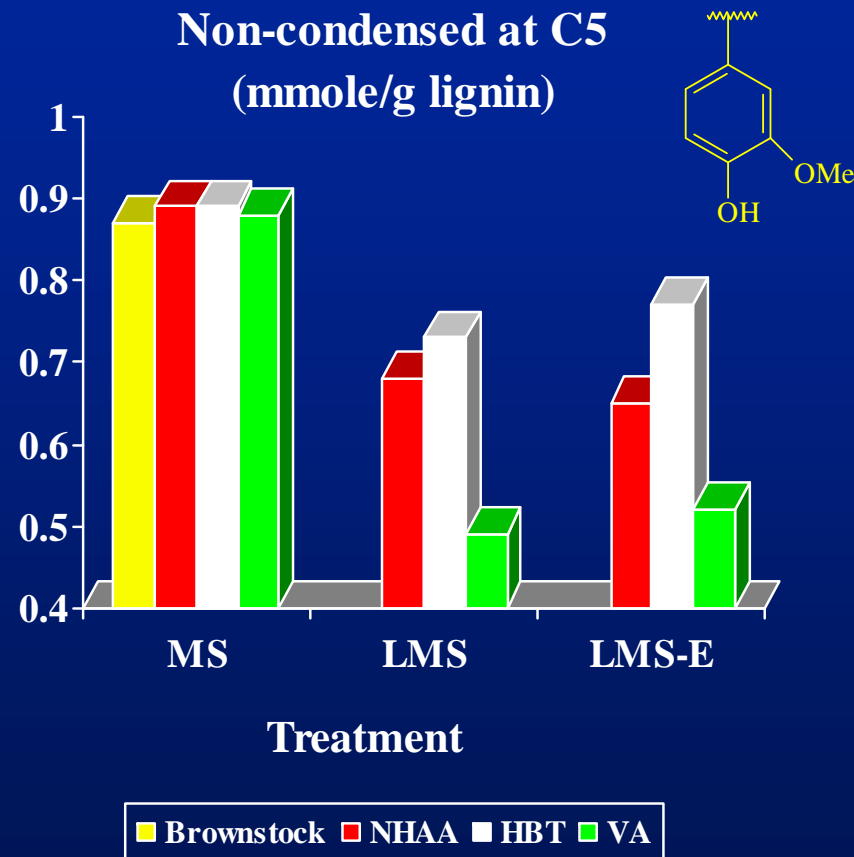


95% LSD=0.032



## *Non-condensed lignin structures at C5*

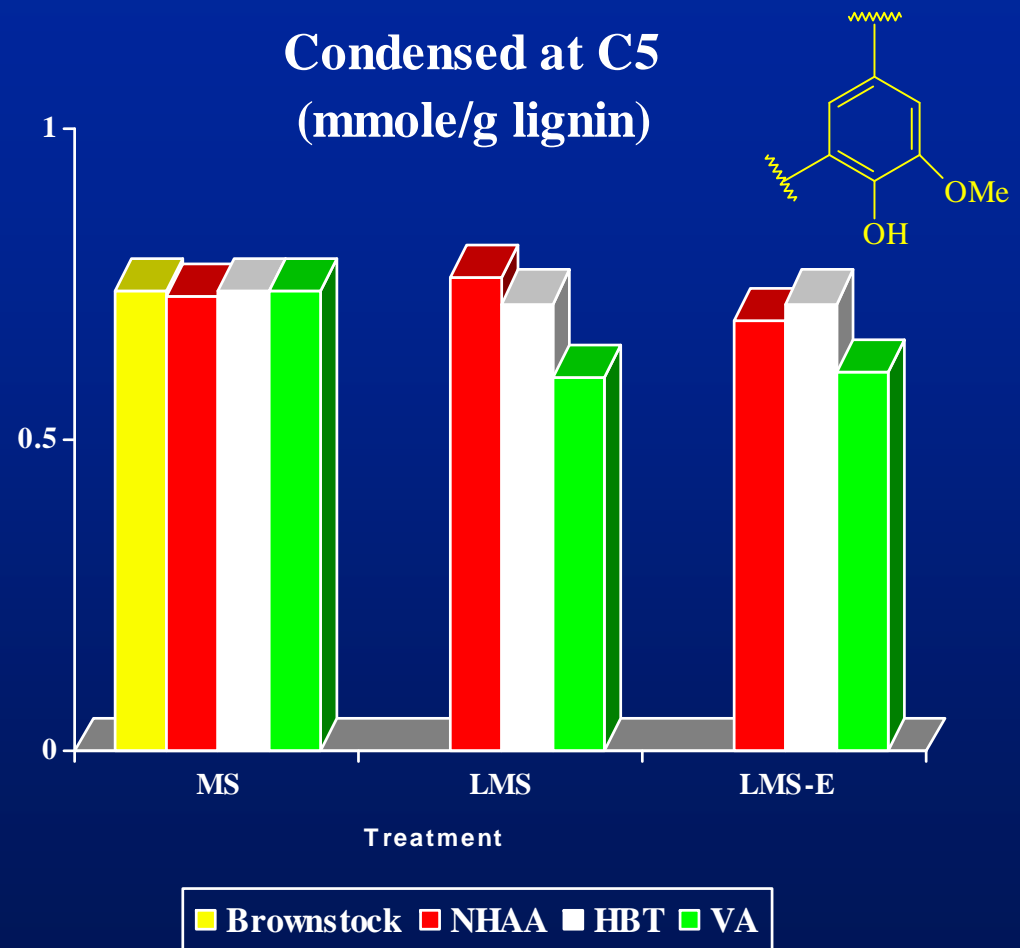
- Depletion with all mediators.
- Largest decrease with VA.
- Decrease greater with NHAA than HBT



95% LSD=0.088

# Condensed lignin structures at C5

- Decrease with VA
- Overall, resistance observed towards condensed structures with HBT and NHAA



95% LSD=0.023

## Quinone content (mmole/g lignin)

- Quinone formation is evident with NHAA, VA, HBT.
- Trend suggest a decrease after E stage.
- Possible explanation for significant increase in brightness after Ep

