

Analysis of Syringyl and Guaiacyl (S/G) ratio in lignin

Presented to SACI

by

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for

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Acknowledgements

- SAPPI
- MONDI
- CSIR
- UKZN

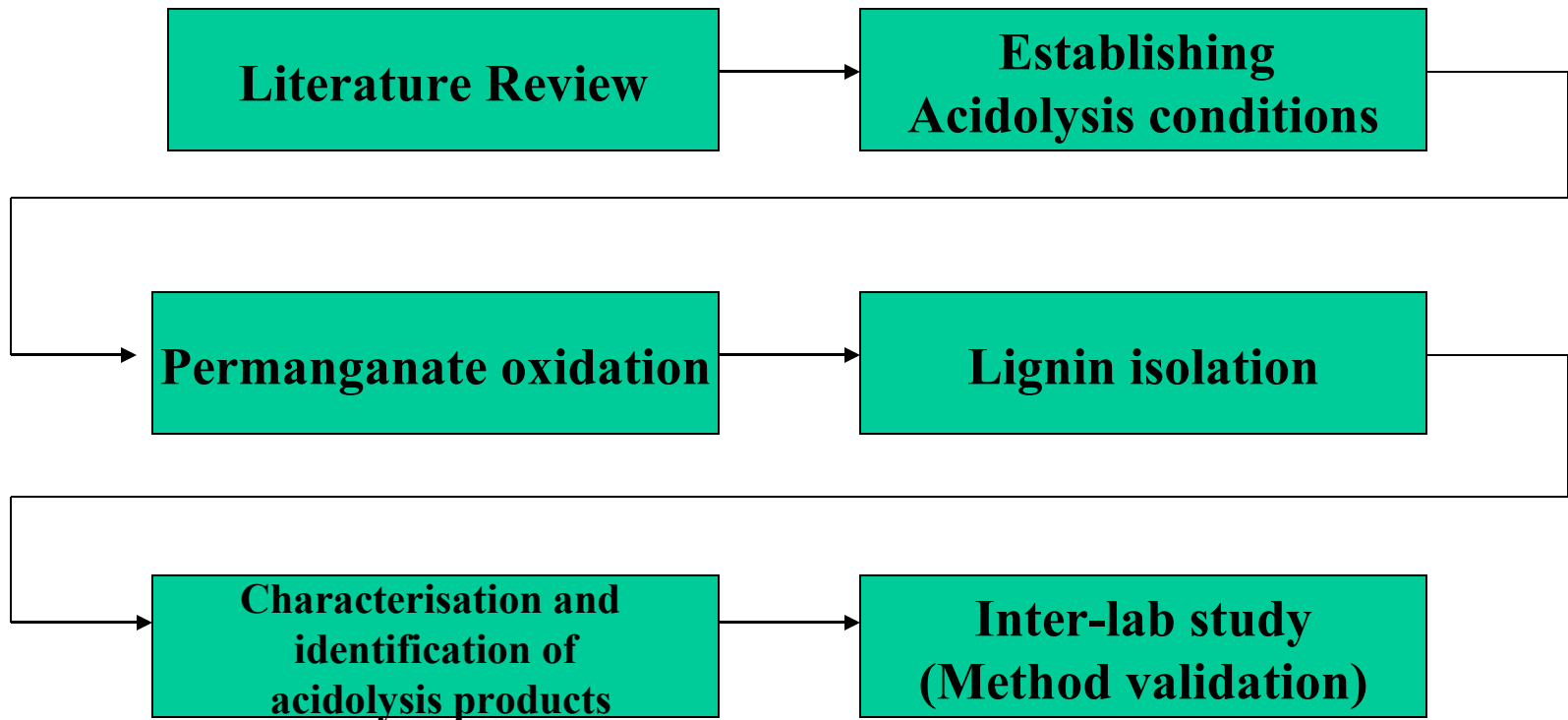
Aim

- Develop a quick and accurate method to measure S/G ratio
- Characterise and identify the acidolysis products
- Validate the new S/G ratio method

Why are S/G ratios important?

- Gives a good indication of the reactivity of the lignin

Experimental design



Introduction

- Lignin is the second most abundant polymeric substance known to man
- Lignin has not been isolated in its pure form which makes both quantitative and qualitative determinations difficult
- Lignin are polymers of phenylpropane units

- Lignin is amorphous

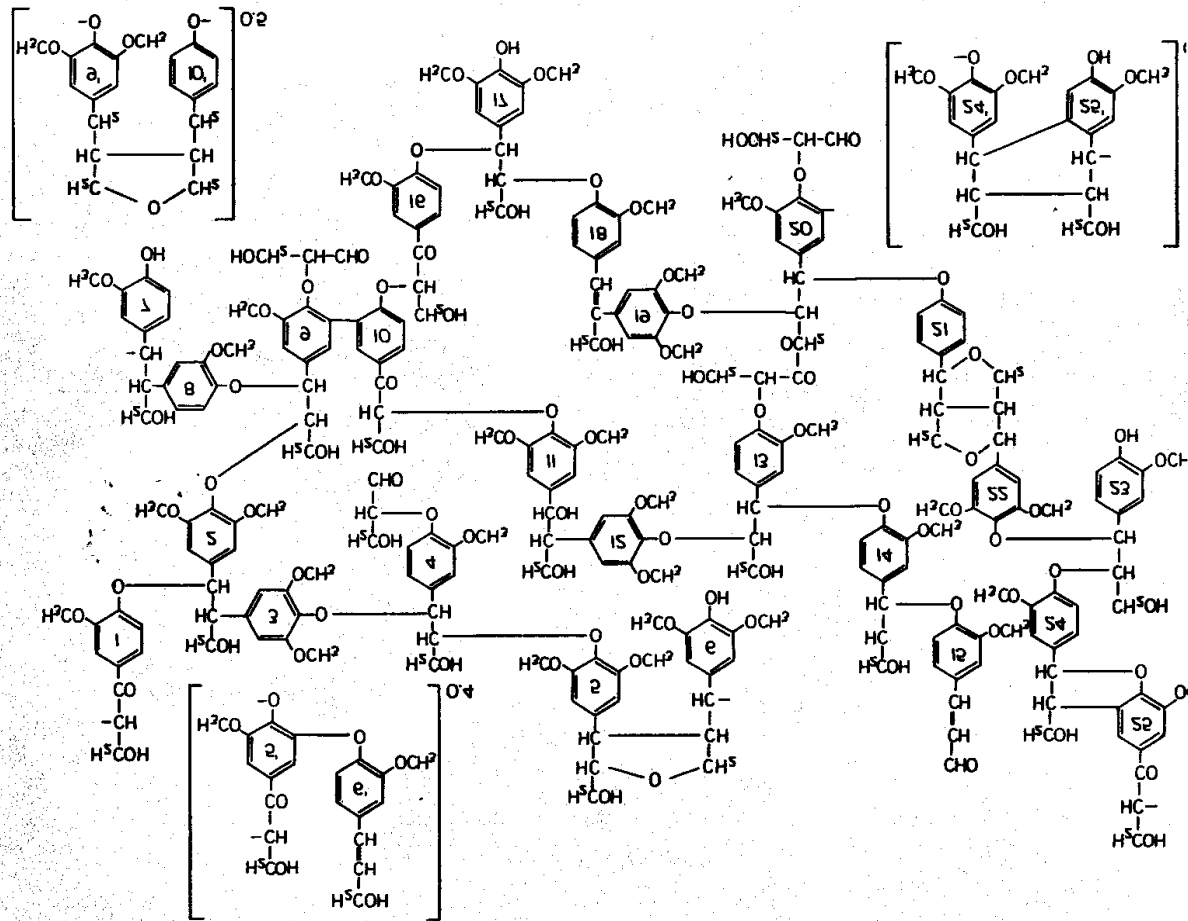
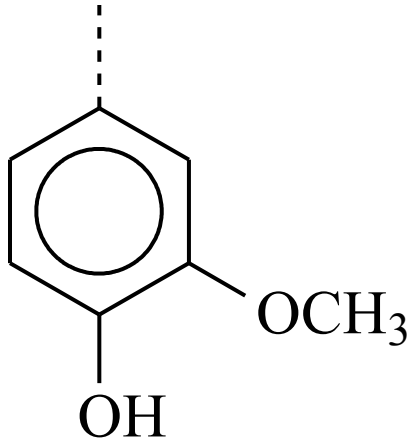


Figure 1: Model structure of lignin (Lin and Dence, 1992)

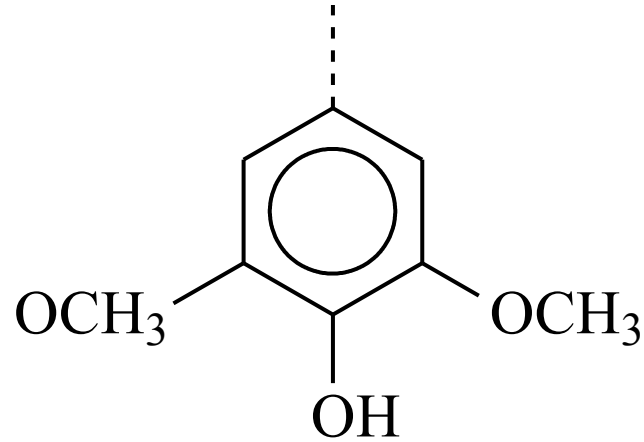
Methods of oxidising lignin into its subunits:

- Acidolysis-method is quick
- Permanganate oxidation-method is slow but it is the standard method used at present
- Nitrobenzene Oxidation, Pyrolysis, Cupric Oxidation and Thioacidolysis

Lignin can be broken down to syringyl and guaiacyl subunits:



Guaiacyl



Syringyl

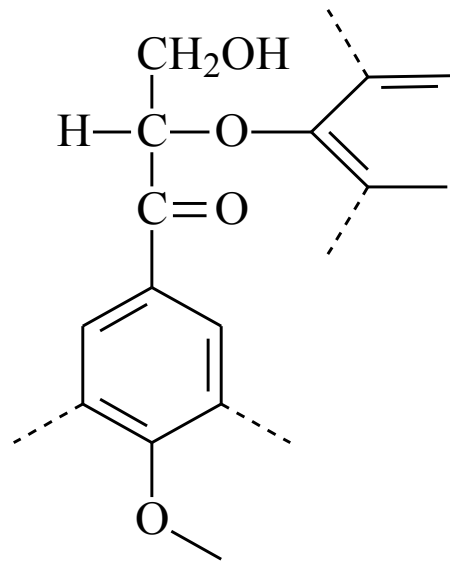
Advantages of Acidolysis

- **Quick** sample preparation times
- Reagents used for the sample preparation are relatively **cheap**
- Sample preparation is **simple**

Acidolysis

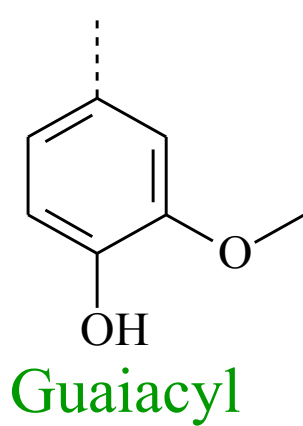
- Present definition-the heating at 105 °C of lignin or sawdust with 0.2 M HCl in dioxane-water (9:1, v/v)
- Acidolysis degradation products are formed by the selective cleavage of arylglycerol- β -aryl ethers and other weak ether linkages

Lignin

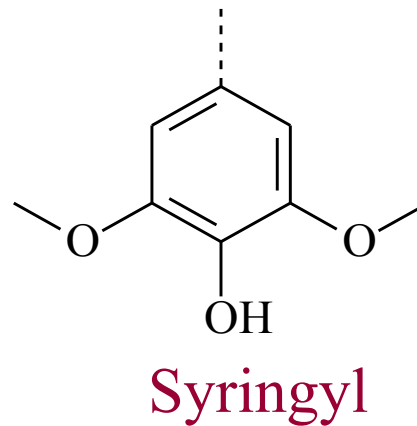


105 °C
4hrs

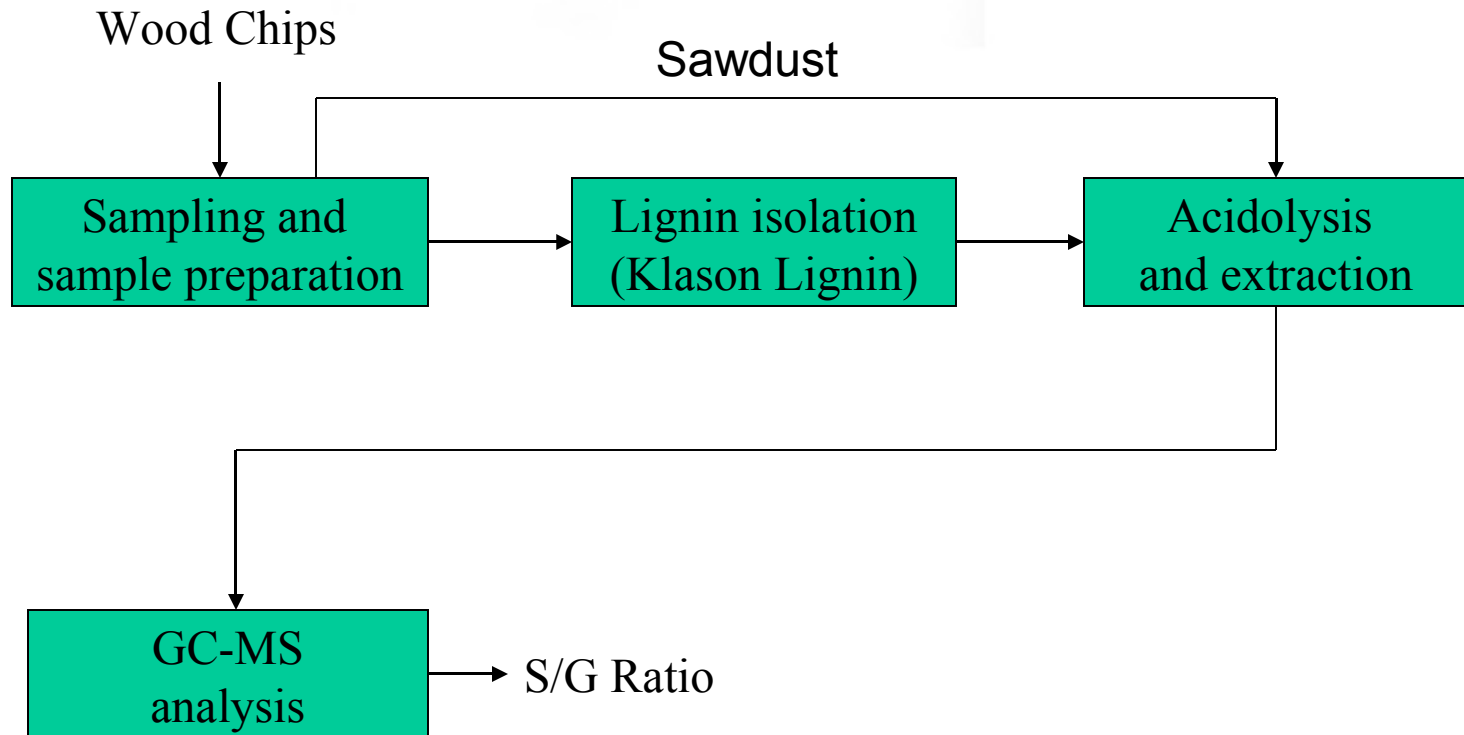
0.2 M HCl



+



Experimental



Results

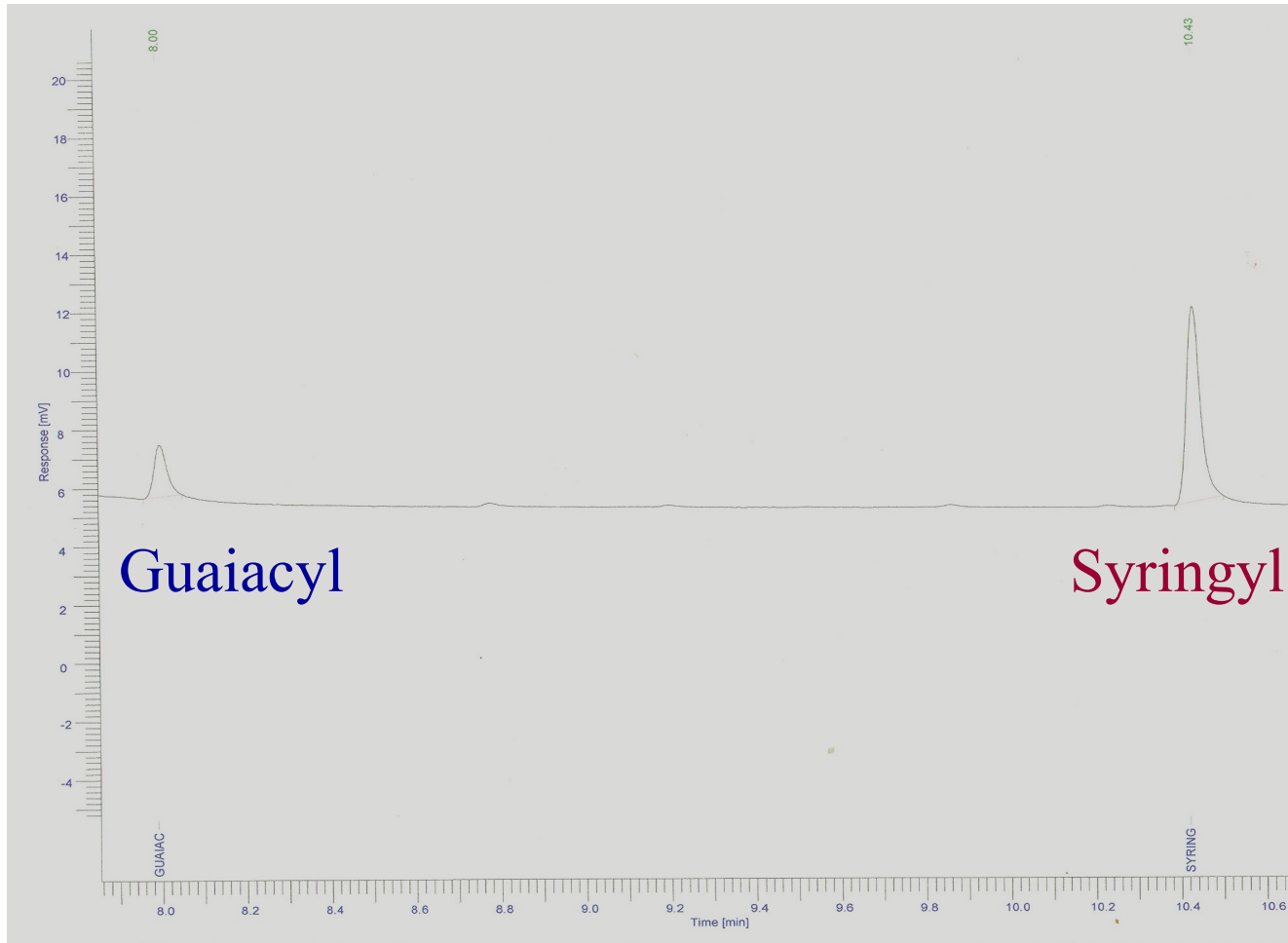
- Acidolysis products were separated using column chromatography
- Characterised and identified using GC-MS together with ^1H -Nuclear Magnetic Resonance (NMR) and ^{13}C -Nuclear Magnetic Resonance (NMR)

Column chromatography

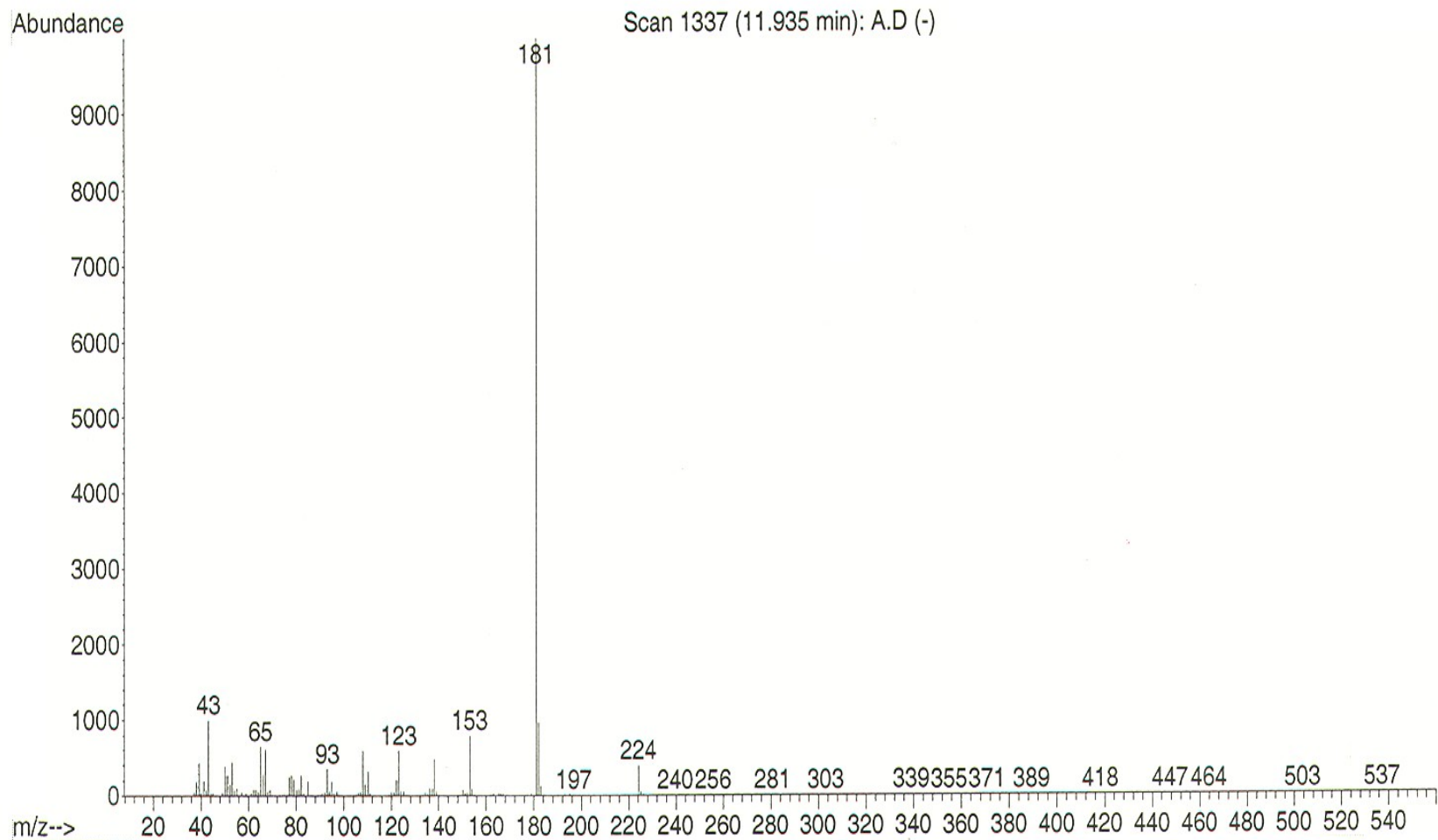
- Solvent system of 15% ethyl acetate and 85% methylene chloride gave the best separation
- Thin layer Chromatography (TLC) was used to determine best eluent

GC Chromatogram

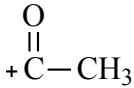
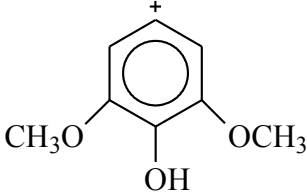
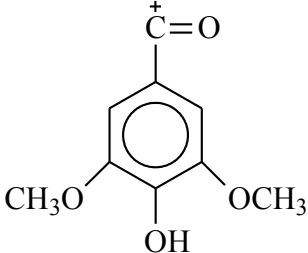
Klason lignin



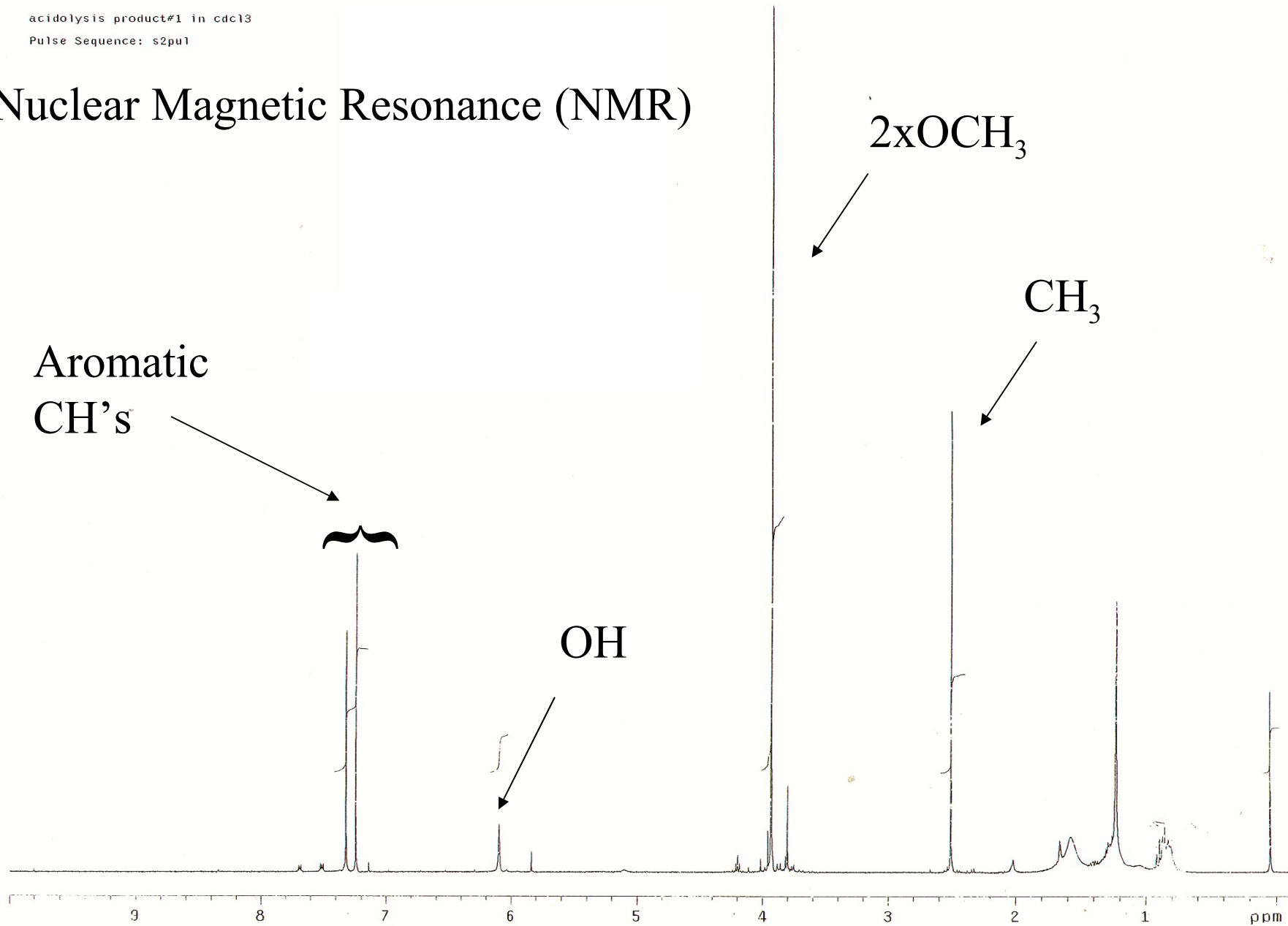
Mass Spectrum of Syringyl



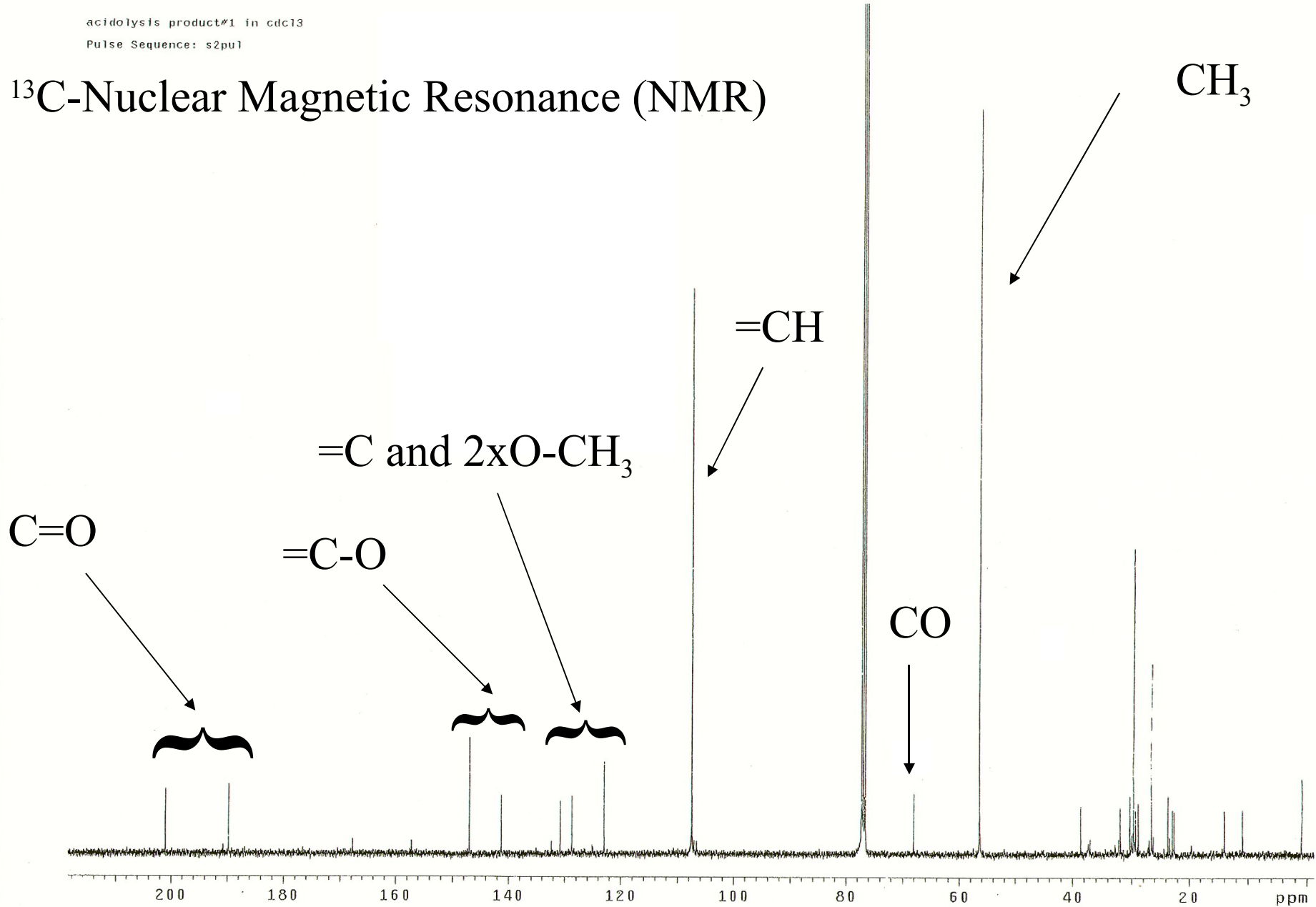
Mass Spectral Analysis of Syringyl

m/z	Fragment
43	
153	
181	

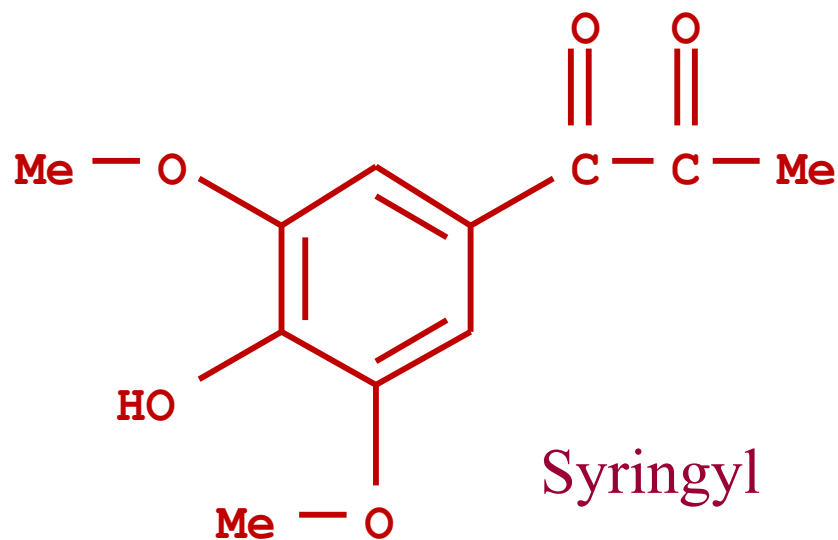
^1H -Nuclear Magnetic Resonance (NMR)



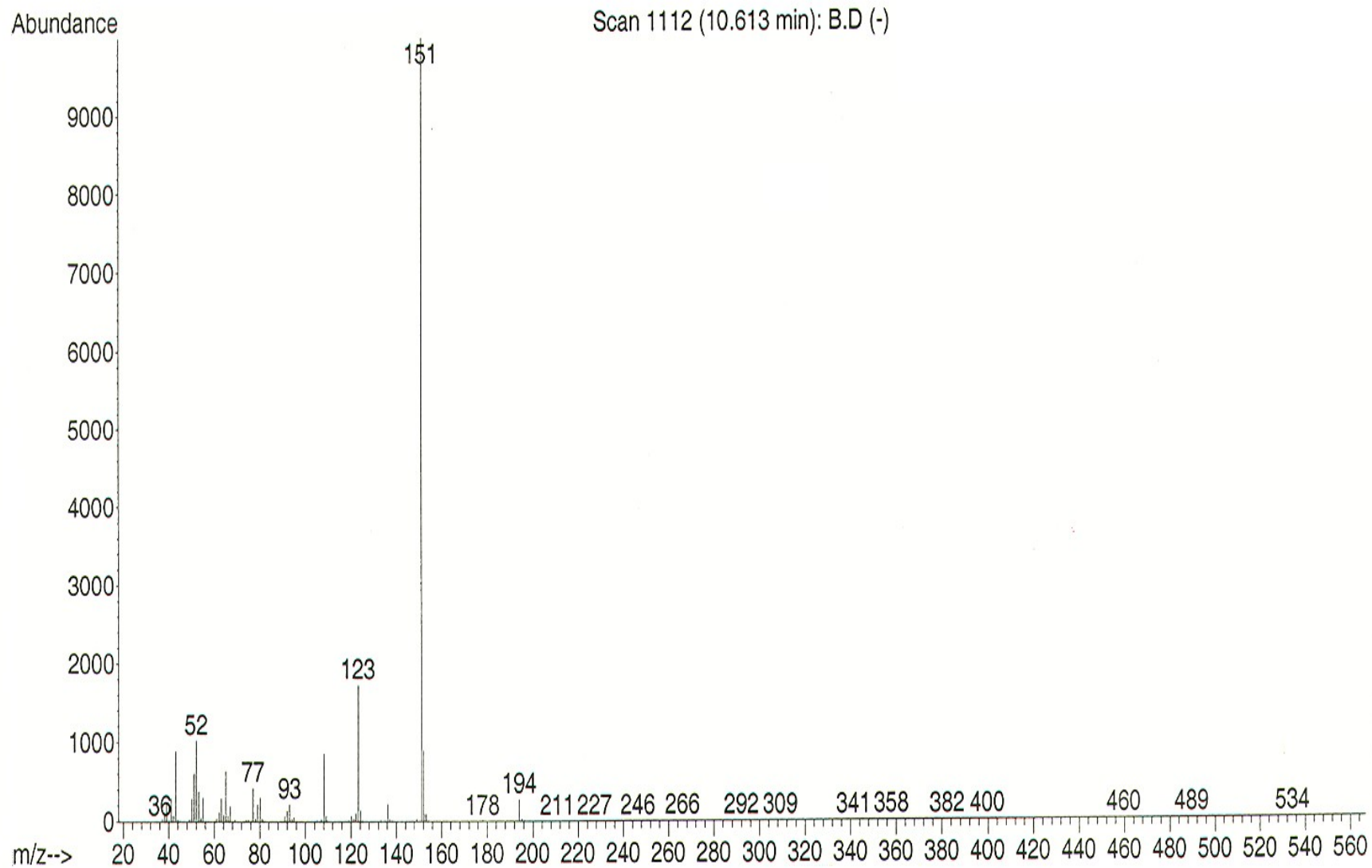
^{13}C -Nuclear Magnetic Resonance (NMR)



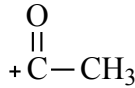
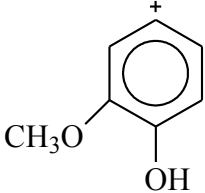
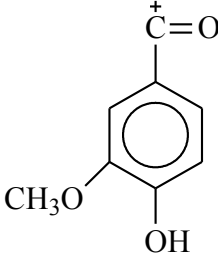
1,2-Propanedione, 1-(4-hydroxy-3,5-dimethoxyphenyl)



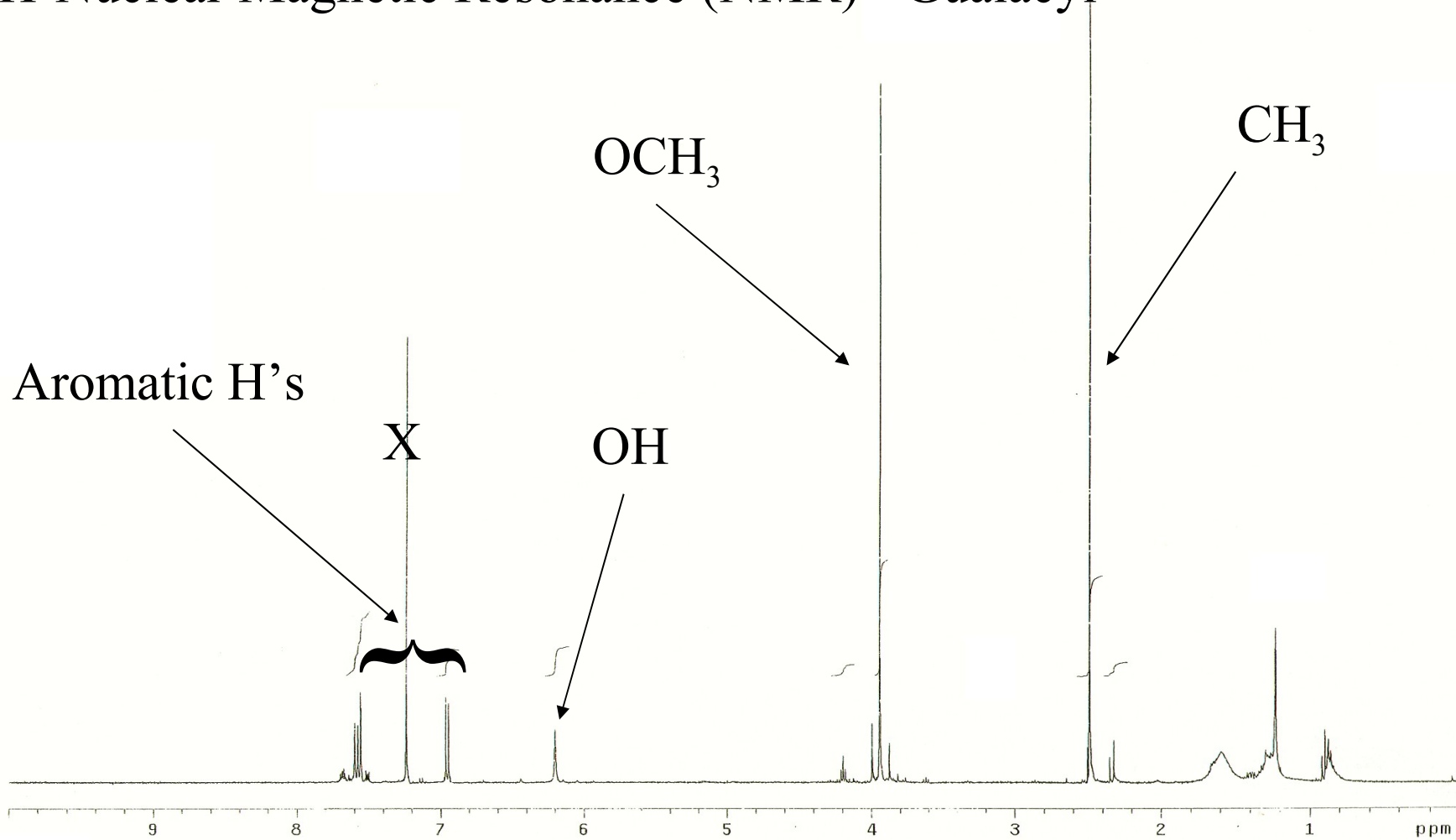
Mass Spectrum of Guaiacyl



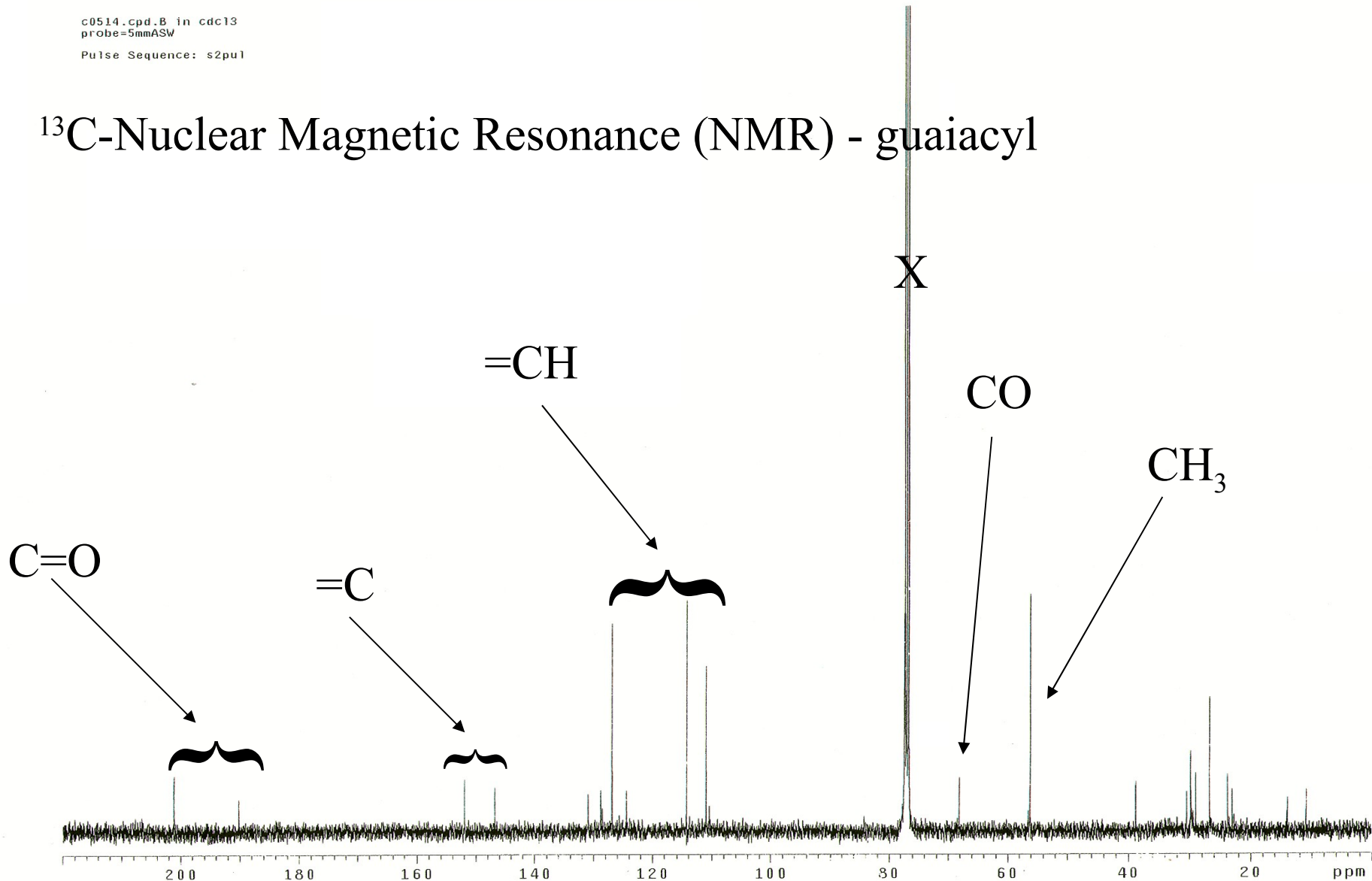
Mass Spectral Analysis of Guaiacyl

Mass/charge (m/z)	Fragment
43	 <chem>CC(=O)[CH2+]</chem>
123	 <chem>COc1cccc(O)[c1+]</chem>
151	 <chem>COc1cccc(O)C(=O)[O+]</chem>

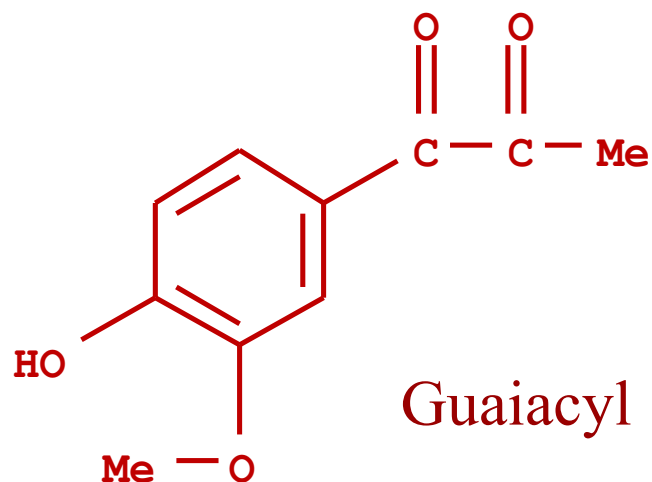
^1H -Nuclear Magnetic Resonance (NMR) - Guaiacyl



^{13}C -Nuclear Magnetic Resonance (NMR) - guaiacyl



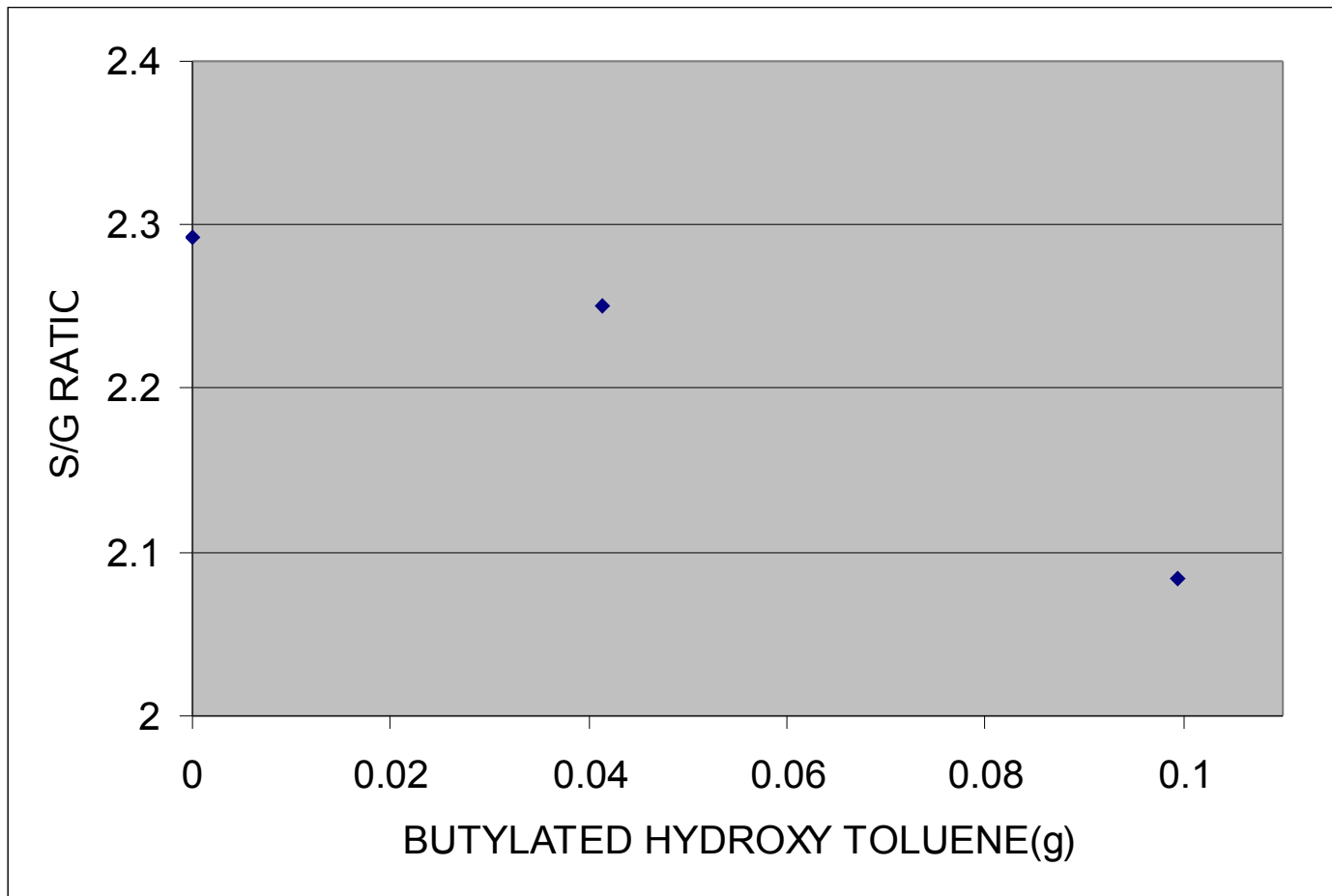
1,2-Propanedione, 1-(4-hydroxy-3-methoxyphenyl)



Repeatability Study

Eucalyptus species	S/G ratio	Standard deviation (4 replicates)
Nitens	2.30	0.04
Dunnii	2.48	0.03
GxC	2.15	0.02
Fastigata	2.50	0.05
Smithii	2.88	0.01
Grandis	2.60	0.05
GxT	1.74	0.06

Internal standard (Butylated Hydroxy Toluene) vs S/G ratio



Klason lignin preparation methods

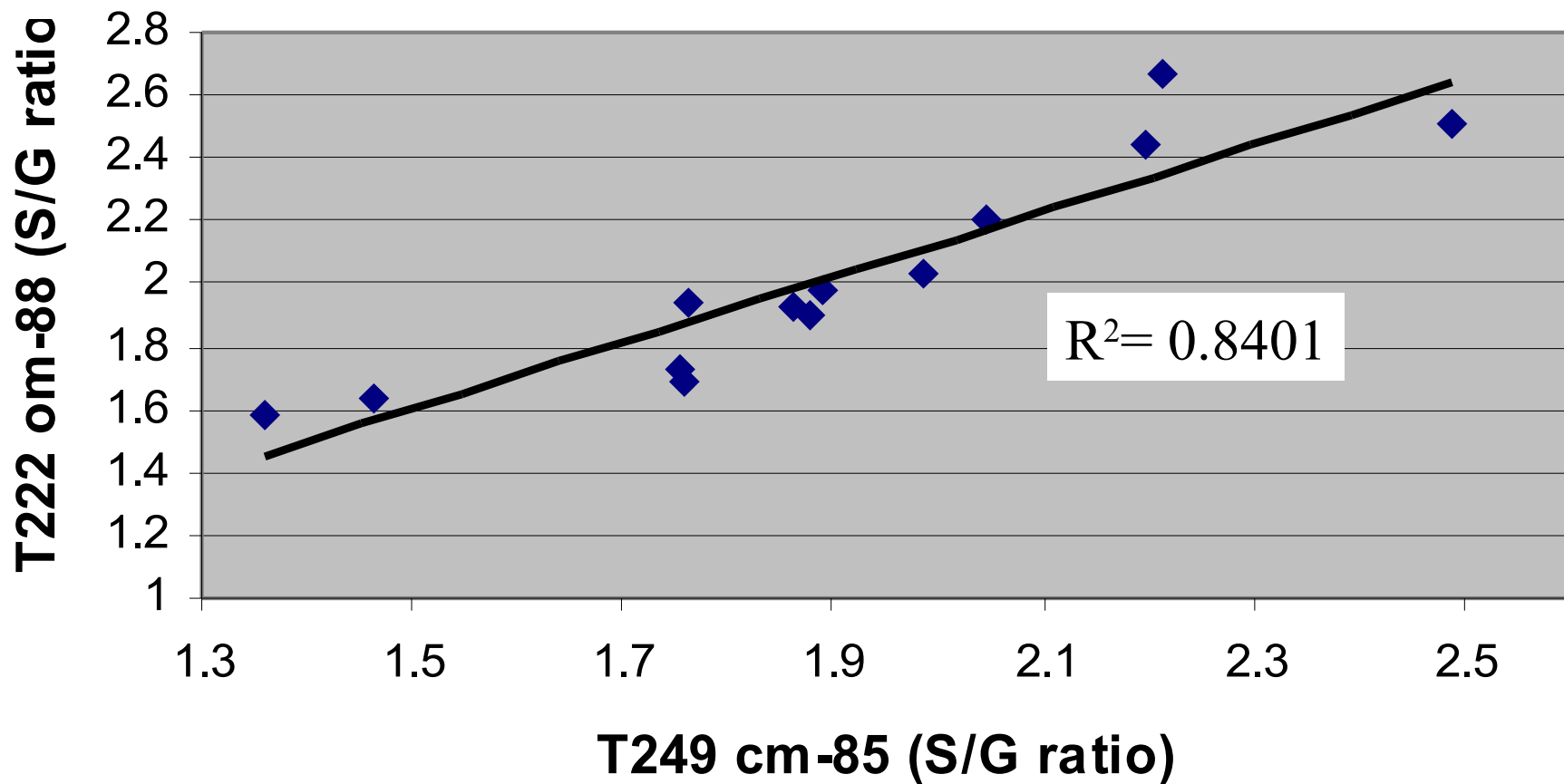
T222 om-88- preparation of
Acid-insoluble lignin
(Klason lignin)

- 15 ml H₂SO₄ (72%) added to 1 g sawdust
- 2 hours at 20°C
- Boil for 4 hours
- Filter off Klason lignin

T249 cm-85- carbohydrate
analysis
(Isolation of Klason lignin)

- 3 ml H₂SO₄ (72%) added to 0.35 g sawdust
- 1 hour in water bath set at 30 °C
- 1 hour in autoclave at 121°C
- Filter off Klason lignin

S/G ratios of Klason lignin from TAPPI method T222 om-88 vs. TAPPI method T249 cm-85



T222 om-88= 6 hours T249 cm-85= 3 hours

Inter-lab. study

- Aim: To compare the **Acidolysis** (CSIR-FFP) method for oxidising lignin with the **Nitrobenzene Oxidation** method used at (Syracuse University, NY)

Comparison of lignin oxidation methods

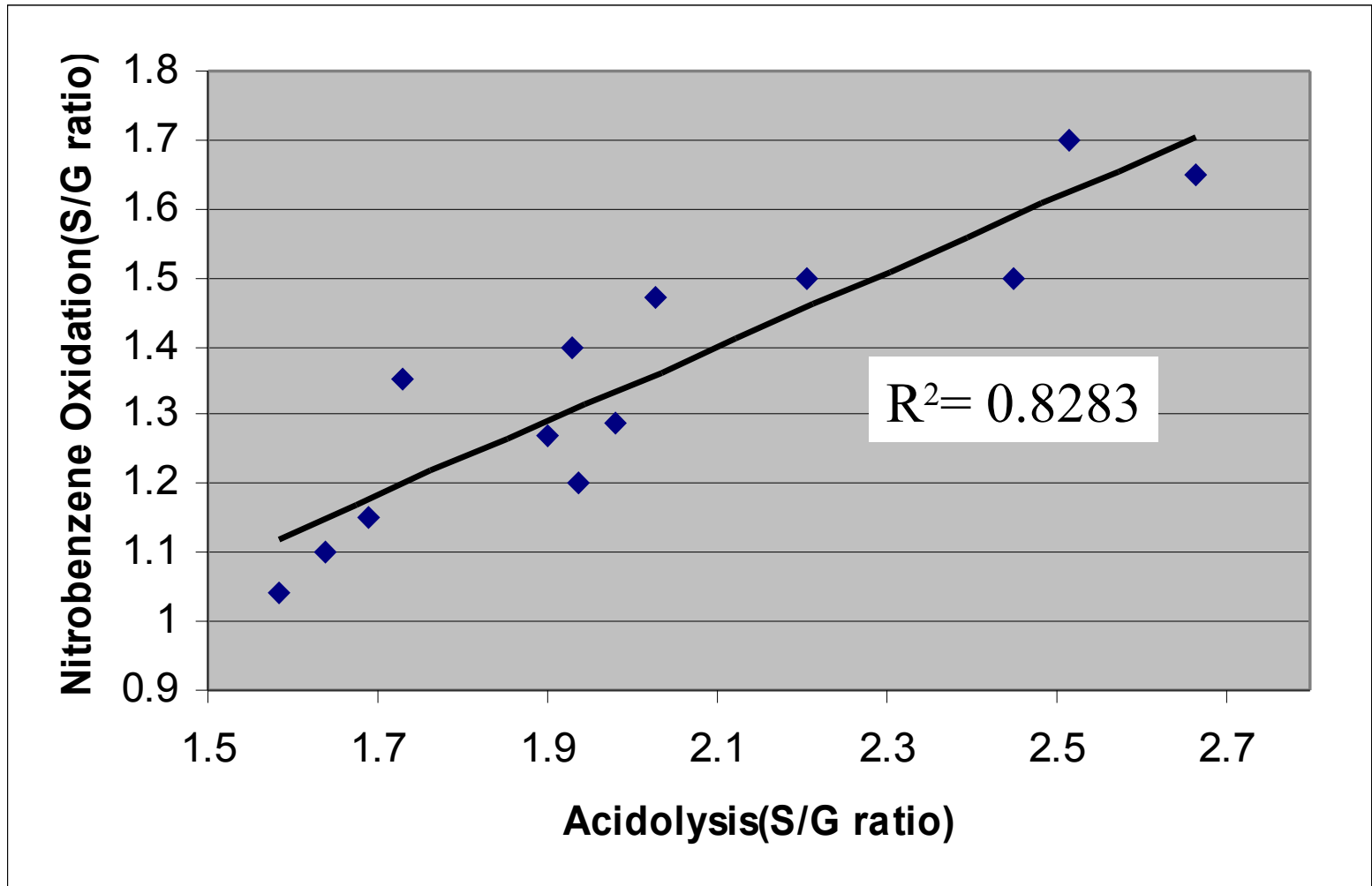
Acidolysis Method

- Acidolysis reagent (2 ml) is added to 0.0150 g Klason lignin
- Acidolysis mixture kept at 105 °C for 4 hours
- Acidolysis mixture is neutralised and then solvent extracted
- Acidolysis products analysed on GC to obtain S/G ratio

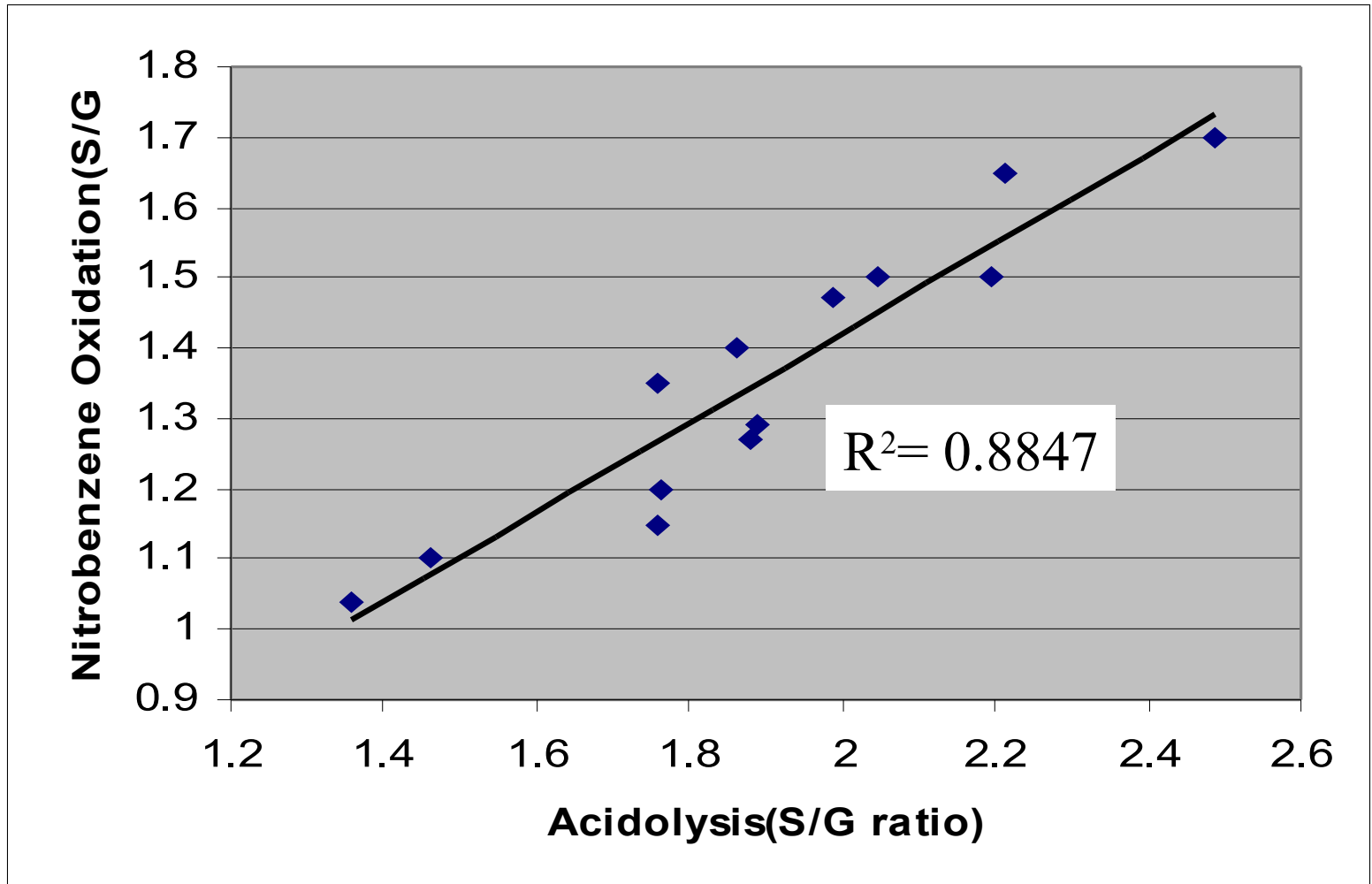
Nitrobenzene Oxidation

- 0.4 g of wood meal is added to a bottle containing 2.5 ml nitrobenzene and 2 M NaOH (40ml)
- Bottle placed in an oil bath (170°C) for 2.5 hours
- 1 hour in autoclave at 121°C
- Autoclave mixture is solvent extracted and the pH is adjusted to 3
- Nitrobenzene oxidation products analysed on the GC-MS to obtain S/G ratio

Comparison of S/G ratios measured using Nitrobenzene Oxidation with Acidolysis (Klason lignin prepared using TAPPI method T222 om-88)



Comparison of S/G ratios measured using Nitrobenzene Oxidation with Acidolysis (Klason lignin prepared using TAPPI method T249 cm-85)



Conclusions

Acidolysis of Klason lignin produces:

- Syringyl unit

1,2-Propanedione, 1-(4-hydroxy-3,5-dimethoxyphenyl)

- Guaiacyl unit

1,2-Propanedione, 1-(4-hydroxy-3-methoxyphenyl)

Conclusions cont.....

- Internal standard BHT plays a major role in preventing the guaiacyl groups from polymerising
- Inter-lab. study was a success with good correlations of the S/G ratios from acidolysis and nitrobenzene oxidation of the lignin

Conclusions cont.....

- The preferred lignin isolation method is T249 cm-85 due to quicker preparation times and better correlation with nitrobenzene oxidation than T222 om-88