



Chloromethylation of lignin as a route towards biomass valorization

Bachelor thesis

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Biomassi väärimine ligniini klorometüleerimise kaudu

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Declaration

I confirm that this thesis has been written by me and that nobody else before me has submitted this for defense. All the work, important stances, written sources, non-written sources from other authors are referenced.

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4. Abstract

Lignin is the second most abundant biopolymer and is a natural source of phenolic compounds. Its structure is random and has many branching within its polymer structure. Lignin is of great interest to organic chemists due to the large quantities that are produced when pulping wood for cellulose and its status as a waste product. Lignin's structure makes it hard to work with and methods to valorize it are being searched for actively.

This thesis is devoted to studying the chloromethylation of lignin, to valorize it in a cheaper and more environmentally friendly way. To achieve a greener reaction, a set of metrics were taken into consideration when choosing and modifying the reactions.

Chloromethylation is an electrophilic substitution reaction discovered by Gustave Louis Blanc, and is known as the Blanc reaction. It is a chemical reaction involving aromatic rings, formaldehyde, and hydrogen chloride with a Lewis acid catalyst to form chloromethyl arenes.

There have been no papers on the successful chloromethylation of lignin, so a new one would have to be found. The value of such a reaction is high, as the chlorine atom makes an easily utilizable reaction site, which makes way for new reactions. This can lead to new lignin-based polymers being developed. Lignin could also be used as a scaffold, due to its size and multiple sites where the chloromethylation reaction could take place, to add other functional groups to.

In this paper calixarenes were used as a model compound due to them being polyphenolic compounds similar to lignin. A new reaction was found that has been used on the model compound and it had much greener metrics than other Blanc reactions. The reaction was confirmed using nuclear magnetic resonance (NMR) and then applied to lignin. The reaction on lignin was confirmed with elemental analysis.

5. Annotatsioon

Ligniin on teine kõige rohkem esinev biopolümeer ja on looduslik fenoolide allikas. Selle struktuur on suvaline ja väga hargnenud. Ligniin on olnud suureks huviks orgaanilistele keemikutele, sest seda toodetakse kõrgetes kogustes puidu töötlemisel tselluloosiks. Seda koheldakse ka kui jääkainet. Selle struktuur raskendab sellega töötamist. Aktiivselt otsitakse võimalusi seda ainet väärindada.

See töö on pühendatud ligniini, kui rikkaliku puidutööstuse toorainena, klorometüleerimise uurimisele, et seda väärindada odavamalt ja keskkonnasõbralikumalt. Rohelise reaktsiooni nimel võeti kasutusele kogum mõõdikuid, mille põhjal reaktsiooni valiti ja muudeti.

Klorometüleerimine on elektrophiilne asendus reaktsioon, mille avastas Gustave Louis Blanc. Seda reaktsiooni tuntakse ka Blanc'i reaktsioonina. See on reaktsioon aroomatiliste tsükliite, formaldehüüdi ja veinikkloriidi vahel. See on katalüüeeritud Lewisi happega ja moodustab klorometüleeritud areeni.

Ligniini eduka klorometüleerimise kohta pole olemasolevaid materjale, seega tuli see väljatöötada. Sellel reaktsioonil on potentsiaalselt suur väärtus, kuna lisatud kloori aatom annab kergesti kasutatava reaktsioonitsentri, mis lihtsustab teiste funktsionaalsete gruppide lisamist. Selline reaktsioon võib viia uute polümeeride sünteesini. Selle suuruse ja mitme reaktsioonitsentri tõttu saab ka seda kasutada alusmaterjalina, mille külge lisada erinevaid funktsiooniga grupe.

Selles paberis kasutati kaliksareene mudelina, kuna see oli polüfenoolne ühend sarnane ligniinile. Potentsiaalne reaktsioon oli mudelaine jaoks olemas. See reaktsioon viidi läbi ja kontrolliti nukle magnet resonantsiga (NMR), positiivse tulemuse järgselt rakendati edukalt ligniinile. Reaktsiooni toimumist kontrolliti elementanalüüsiga

6. Abbreviations

AE – atom economy

CML – chloromethylation

DMF – dimethyl formamide

G - guaiacyl

H - p-hydroxyphenyl

NMR – Nuclear Magnetic Resonance

OE – optimum efficiency

PDI – polydispersity index

ppm – parts per million

RME – reaction mass efficiency

S – syringyl

TMS - tetramethylsilane

XRF –X-ray fluorescence

7. Introduction

Lignin is an abundant biopolymer, that is found alongside cellulose and hemicellulose in the structure of wood. It is the second most abundant biopolymer, behind cellulose. It makes wood tough and brown. It is a natural source of aromatic phenols. It is synthesized within the plant from p-coumaroyl alcohol, coniferyl alcohol and sinapyl alcohol. Its structure is random, even within the same species of plant. Lignin that is separated from wood is created mostly as a byproduct of the papermaking industry and is burned as low-grade fuel.

Lignin is of interest to scientists due to its abundance and composition, but its large structure, that is dependent on many factors such as the growth conditions, species, age of the plant, and even the way it was extracted. This affects many of its properties, such as solubility (which is usually poor), the ratios of the monolignols and how the bonds connect them, this makes it hard to utilize as is, so it has been broken down to smaller phenolic compounds and some modifications have been made to the larger structure. But if the environment is to be considered, which has become a more important issue in many fields, including chemistry, breaking it down into smaller units is wasteful and uses reactants that aren't sustainable. In green chemistry emphasis is put on using environmentally friendly solvents, renewable reactants and effective reactions with good yields and selectivity.

A new sustainable reaction that modifies the lignin polymer is an important step towards the goal of valorization, to aid in finding value in the larger structure rather than just its carbon content as a fuel or small fragments as a precursor.

The goal of this paper is to research the chloromethylation reaction of aspen organosolv lignin, that can be used to further modify the lignin polymer to create new added value. If this reaction is successful, it creates new possibilities in the modification of the compound. Allowing easier and less environmentally taxing modification, with possible industrial application in the future.

8. Literature review

8.1. Lignin

8.1.1 Structure

Lignin encompasses a group of polyphenolic polymers. These molecules are found in the cell walls of plants in the vascular phyla, which together with hemicellulose and cellulose form the plant cell wall. Lignin is what makes the cell wall brown and gives it its toughness¹ It is one of the most abundant biomolecules, only being second to cellulose. It shows antimicrobial and antioxidant properties. It even waterproofs some cells, due to the low water solubility of the monolignols.²

The polymer is irregular, and its properties depend on the ratios on linkages between the monomers, which themselves depend on the species of plant. The monolignols are H (*p*-hydroxyphenyl), G (guaiacyl) and S (syringyl). Hardwood lignin has 90% G and traces of H, while softwood lignin has no S unit and is composed only of G and low levels of H. Grasses have equal G and S and the highest H levels of the two priors.^{1,3}

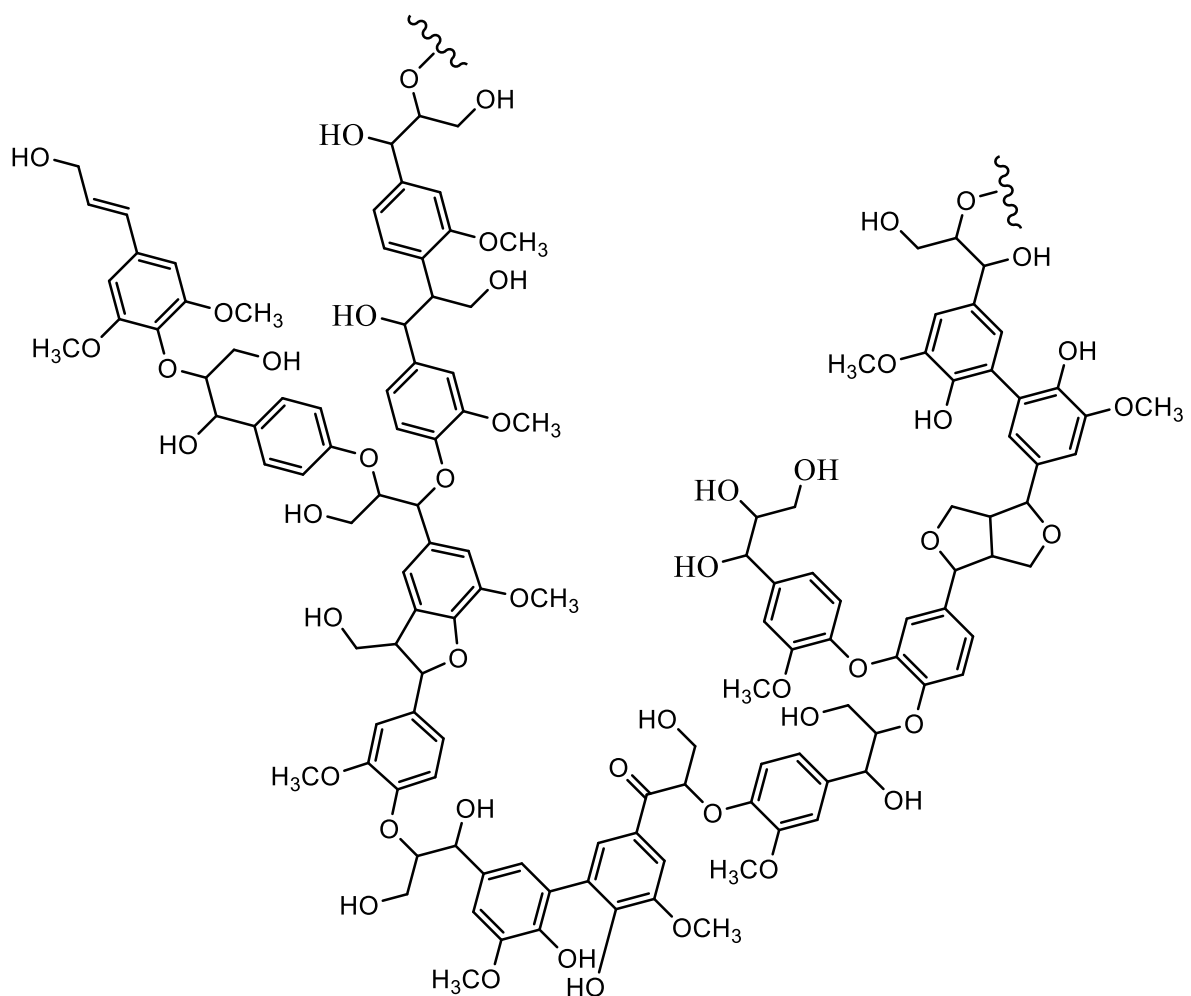


Figure 1.1 A schematic representation of lignin³

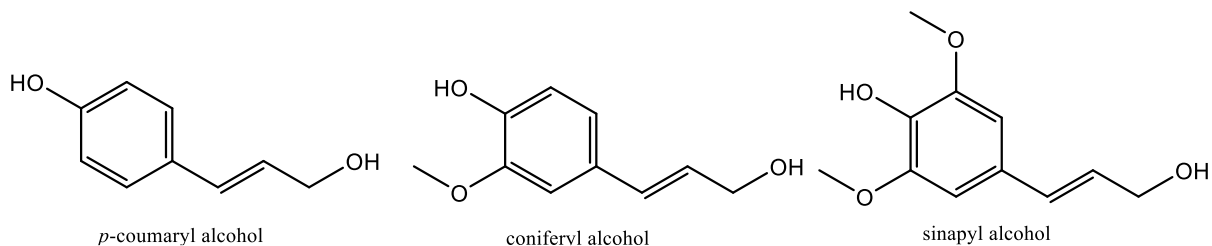


Figure 1.2 Building blocks for lignin monolignols³

The content and structure of lignin differs between species, it varies between 15-30%. Even the same species of plant has variance due to age and cell type. The lignification process isn't fully understood and thus it is hard to precisely predict a specific lignin's properties and amount contained in each plant.^{2,4}

Lignin is created in the enzymatic polymerization of the monolignols, forming H from p -coumaryl alcohol, G from coniferyl alcohol and S from sinapyl alcohol. They link together in several different ways as seen in Table 1.2 and Figure 1.3.³

Type of linkage	Softwood lignin (%)	Hardwood lignin (%)
Arylglycerol- β -aryl ether (β -O-4)	46	60
Phenylcoumarine (β -5)	11	6
Noncyclic benzyl aryl ether (α -O-4)	7	7
Biphenyl (5-5)	10	5
Diaryl ether (4-O-5)	4	7
1,2-Diarylpropane (β -1)	7	7
Resinol (β - β)	2	3
Others	13	5

Table 1.2 Distribution (in %) of the different linkages in lignin, as determined by various methods³

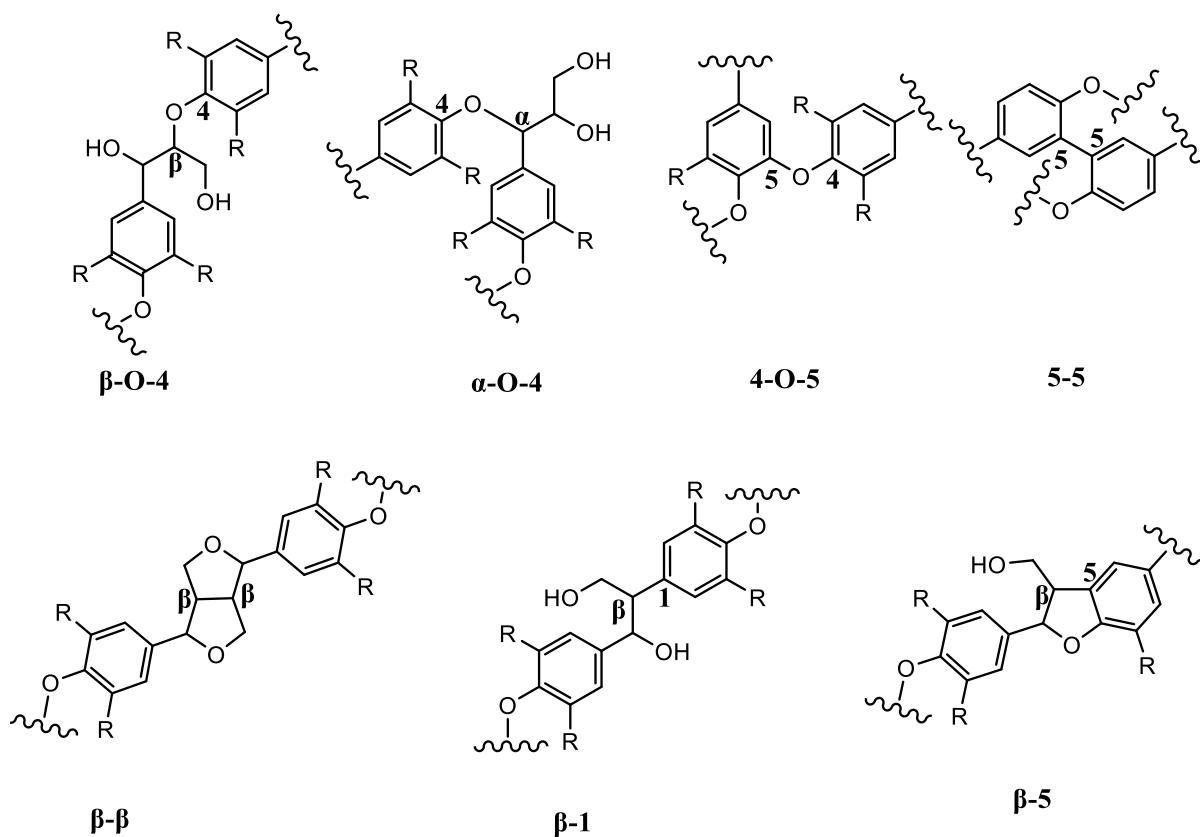


Figure 1.3 The most dominant linkages in lignin³

8.1.2 Solubility

Lignin can be categorized into two broad groups: soluble and insoluble. The group into which the lignin falls depends on the extraction method, which breaks down and reacts with the lignin differently. The smaller the fragments, the more soluble it is in standard solvents. Some chemical modifications also influence this along with the structure of the original polymer. The more soluble fragments are sought after due to them being easier to chemically process and allow for a wider choice of potential reactions.⁵

8.1.3 Organosolv Method

Organosolv is one of the non-industrial methods used in research lab settings, and it yields lignin whose structure is more intact and is soluble in standard solvents. A reflux system with a chosen organic solvent will separate the smaller soluble fractions from the larger insoluble ones. The ones with the most promising indicators are ethanol and dioxane.⁵

Lignin ID	Solvent	Lignin Yield %	M _w	M _n
EOL-Aspen	Ethanol	15 ± 2	1925	2670
DOL-Aspen	Dioxane	44 ± 6	22187	3211

Table 1.4 Molecular weight of organosolv aspen lignin⁵

8.1.4 Kraft Process Lignin

In the most widespread process, the Kraft process, lignin is a byproduct, which means the intactness of the lignin isn't a priority. The main function of this reaction is the extraction of cellulose from wood. The active ingredients in this process are sodium hydroxide and sodium sulfide, which dissolve half the wood, leaving behind the cellulose. This pulp makes up two-thirds of virgin pulp and 90% of chemical pulp. The dissolved fraction is then washed out, creating black liquor. It is highly effective with a recovery rate of 97%.⁶ The produced lignin is sulfurous in nature, containing 2-3% by weight.⁷

The used chemicals are recovered, and the residual weak black liquor is concentrated. The resulting heavy black liquor is used to generate steam to produce electricity and provide energy to the reclamation of sodium hydroxide and sodium sulfide. This makes black liquor the fifth most important fuel in the world.⁶

Kraft lignin is known to be soluble in polar aprotic solvents, which include dimethylformamide (DMF), dimethylacetamide (DMAc) and DMSO. It is also soluble in hexane, diethyl ether, dichloromethane and dioxane. However, these solvents are considered undesirable in industrial settings, due to safety, environmental and regulatory reasons. This would leave alcohol-based solvents, acetone, butanone (MEK), and ethyl acetate (EtOAc) as potential solvents in an industrial setting. The solubility, however, does not go above two-thirds. Table 1.5 also shows how the larger fragments make up the insoluble fraction.⁸

Solvent type	Solvent	Solubility (%)	Soluble fraction			Insoluble fraction		
			M _n (g mol ⁻¹)	M _w (g mol ⁻¹)	PDI	M _n (g mol ⁻¹)	M _w (g mol ⁻¹)	PDI
Alcohol	MeOH	61.2	580	2040	3.52	3860	14120	3.66
	EtOH	46.8	460	1400	3.04	3200	10710	3.35
	1-propOH	34.5	280	790	2.82	1500	7800	5.20
	<i>i-propOH</i>	14.9	290	760	2.62	1150	6720	5.84
	t-buOH	8.0	260	780	3.00	650	5670	8.72
Ketone	Acetone	66.5	620	2450	3.95	4070	15760	3.87
	MEK	55.4	320	1300	4.06	1870	10390	5.56
Ester	EtOAc	28.0	300	710	2.37	1900	7800	4.11

Table 1.5 Yields of the soluble fraction and average M_w and polydispersity of the fractions⁸

8.1.5 Soda Process

The soda process uses different alkali solutions (ammonium, sodium, calcium hydroxide), but mostly sodium hydroxide, to extract the lignin from the biomass. This is done at a variety of temperatures. A very important step for this process is pretreatment with different compounds (ethanol, formic acid, hexane, acetic acid, and others), which effect the overall environmental impact of the process.⁹

8.2. Chloromethylation of Arenes

Chloromethylation for arenes is usually done with the Blanc reaction¹⁰ using Lewis's acid catalysts (ZnCl₂, SnCl₄, AlCl₃, BF₃, FeCl₃, TiCl₄) and an organic solvent (chloromethane, acetic acid, carbon tetrachloride, dichloromethane, carbon disulfide, chloromethyl ether). Additionally, a source of formaldehyde (formalin or paraformaldehyde) and hydrogen chloride is required. It is a typical electrophilic substitution reaction.

8.3. Lignin Chloromethylation Using Greener Method

Green chemistry principles require renewable feedstock and reagents, nontoxicity, degradability in the environment for less molecularly complex molecules and maximal functionality.¹¹

Following the Green Chemistry principles, the variation of the Blanc reaction requires minimizing the use of Lewis acids (catalysts are made of non-renewable rare-earth metals), optimization of the energy consumption (running at the room temperature and normal atmosphere) and choosing greener alternative to the problematic organic solvents (toxicity and environmental impact of their production).¹² An advantage of the Blanc chloromethylation of lignin would also be the introducing chloromethyl groups to the aromatic rings while the OH-groups will remain intact (unsubstituted).

Although the Blanc reaction, a chemical method to form chloromethyl arenes with formaldehyde and hydrogen chloride catalyzed by Lewis's acids¹⁰ is widely used for about 100 years, no evidence of its successful application to lignin was found in literature, to the best of our knowledge. At the same time, chloromethylation with no Lewis acids were reported for a model compound for syringyl monolignol unit (Fig. 1.2), 3,5-dimethyl-4-hydroxyphenyl ethane¹³ and for aromatic macrocycles, calix[4]arenes.¹⁴ As the lignin analogue, in this work, calix[4]arenes were chosen to confirm the greener procedure for the chloromethylation of lignin and transfer this knowledge to the organosolv aspen lignin.

8.4 Calixarenes

Calixarenes are cyclic oligomers of phenols which usually consist of 4 to 8 phenolic repeating units. These compounds are a very popular building block for molecular chemistry and materials, which include catalysis, nano particle synthesis, biological applications and so on.

They are obtained by base-catalyzed condensation between appropriate p-functionalized phenols with formaldehyde or paraformaldehyde.¹⁵

8.5 Nuclear Magnetic Resonance

NMR detects atomic nuclei and gives us information about what kind of environment it is in. It detects either ^1H or ^{13}C nuclei depending on the mode. It uses this information to distinguish the nuclei. It is a very versatile method. It can be used to identify unknown compounds. Samples are prepared in an appropriate solvent that does not interfere with the machine and is put in a narrow tube, which is then spun in the machine to even out any imperfections.

Detection takes place under a very strong magnetic field which the magnetic nuclei (which ^{13}C and ^1H are) react to and align themselves according to it. The energy being in a higher state if it aligned more against the field. This alignment causes a measurable change of energy level which can be measured, in a weak magnetic field the differences would be too low to measure.

The energy level is measured using radio waves, the nuclei absorb it, go to a higher energy state. Once the radio waves stop, it flips back to its lower energy state and gives a small pulse of electromagnetic radiation. The machine then calculates the intensity of each signal.¹⁶

The reason the nuclei can be differentiated is that each nuclei have a different number of electrons surrounding them, which affect its magnetic field by shielding it from external fields and thus the signal it gives out. This effect is called the chemical shift and can be used to identify the peaks in the results. There are four regions for ^{13}C NMR. Within 200-150 ppm there are unsaturated carbon atoms next to oxygen, 150-100 ppm unsaturated carbon atoms, 100-50 ppm has saturated carbon atoms next to oxygen and then 50-0 ppm has saturated carbon atoms.

^1H nuclei only have 2 regions in their respective NMR. Starting from 10-5 ppm H atoms bonded to unsaturated carbons and 5-0 ppm H atoms bonded to saturated carbons.

A reference sample is used to calibrate the signal, usually tetramethyl silane (TMS) is used, but other possible options exist.¹⁶

8.6 X-ray Fluorescence

XRF is a non-destructive qualitative and quantitative analytical method used for element analysis. The sample has one of its inner orbital electrons excited by a primary X-ray source (X-ray tube). When the gap left by the dislodged electron is filled by another from a higher energy orbital, a secondary fluorescent X-ray is emitted. This energy is then measured. The elements can be differentiated due to each element having a unique set of secondary X-rays.¹⁷

9. Goals

Based on the literature review, the following goals were set for this research paper.

- Use 5,17-dioctyloxy-1,3-dihydroxycalix[4] as a model compound
- Synthesize a new type of lignin polymer using chloromethylation
- Calculate the green chemistry metrics of the chloromethylation reactions
- Compare the old chloromethylation reaction with the new reaction
- Analyze the future uses of the potential new polymer

10. Materials and methods

10.1. Chemicals

The used reagents and chemicals from Sigma-Aldrich were of analytical grade and used as is. Deionized water was produced by a Milli-Q water purification system. The calixarene 5,17-dioctyloxy-1,3-dihydroxycalix[4]arene was prepared by Oleg Silenko, PhD. Aspen wood chips were provided by Estonian Cell AS.

10.2. Organosolv Extraction of lignin

The provided aspen wood chips were dried and ground, 50 g of the powder was refluxed in a reflux condenser, using 1.5 l of 0.28M HCL in a 95%v/v ethanol and water mixture, for 6 hours in a 2.0 l round bottom flask. The solids were filtered out using Whatman filter paper, and then washed 3 times using 50 ml doses of ethanol. The liquid phase was then concentrated to 100 ml by rotor evaporation. The powder was precipitated out of the solution by dissolving it in an equal volume of acetone and then poured into 2 l of cold deionized water. The mixture was then vigorously stirred for 60 minutes. The precipitate was extracted using centrifugation at 4300 rpm. The recovered solids were then washed 3 more times using 1 l of deionized water and finally dried at a convection oven at 30 °C for 24 h.⁵

10.3. Chloromethylation of the model compound

Based on the procedure outlined by Burilov et al¹⁴, 0.63 g of 5,17-dioctyloxy-1,3-dihydroxycalix[4]arene along with 0.64 g of paraformaldehyde were added to a 100 ml two-necked flask along with a magnetic stirring bar. Then 10 ml of glacial acetic acid was added to the flask and the contents were stirred using the magnetic stir bar until suspended. Gaseous HCl was bubbled from a hydrochloric gas generator (conc H₂SO₄ reacting with NaCl under constant heating) for 2 hours and stirred, any excess HCl was captured and neutralized in a beaker filled with a concentrated solution of sodium hydrogen bicarbonate. The reaction was stopped by adding 30 ml of distilled water. It was then refrigerated for 2 hours. The powder was then washed and filtered 3 times with water and once with 30 ml of methanol, all in a separatory funnel. The resulting white powder was then dried in vacuo.

10.4. Chloromethylation of lignin using Blanc reaction

15 mmol of methyl chloromethyl ether was added to a solution of 1 gram of organosolv aspen lignin prepared according to the known procedure⁵ in 20 ml of dry chloroform. The resulting solution was cooled using dry ice to -60 °C in an argon atmosphere. 2 mmol of titanium tetrachloride was added dropwise to the mixture under vigorous stirring. The reaction mixture was then stirred on a magnetic stirrer for 30 min at -60°C, after which the mixture was allowed to reach room temperature. 15 ml of deionized water and the same volume of CH₂Cl₂ was added to the mixture and stirred until the color faded. The organic layer was separated using a separatory funnel, and then washed with 3%

hydrochloric acid (20 mL) and deionized water (20 ml) inside the funnel. It was dried overnight using sodium sulfate and resulted in a brownish powder.¹⁸

10.5. Chloromethylation of lignin with new method

In line with green chemistry principles a modified variation of the reaction used on the model compound was performed. 1 gram of organosolv aspen lignin, prepared according to the known procedure⁵, and 1 g of paraformaldehyde were suspended in 15 ml of glacial acetic acid in a two necked flask along with a stir bar. HCl gas was then bubbled into the reaction from a gas generator (same method as for the model compound) for 2.5 hours, any excess was captured and neutralized in a sodium hydrogenbicarbonate solution. The reaction was stopped with 35 ml of deionized water. It was then left stirred for 15 minutes with a magnetic stirrer. After it was filtered 3 times with a 10% acetic acid solution (3 x 10 ml) and 3 times with water (3 x 20 ml) and then dried using a vacuum for 2 hours at 0.05 mbar and yielded a brownish solid.

10.6. NMR characterization

The chloromethylated calix[4]arene and chloromethylated lignin using the new method were both analyzed using NMR (Bruker Avance III 400 MHz) and processed using the MestReNova x64 software to confirm that the reactions took place.

About 35 mg of the chloromethylated products were each dissolved separately in 600 μ l of CDCl₃. The calix[4]arene underwent proton analysis at 400 MHz and the lignin underwent ¹³C NMR analysis at 101 MHz.

10.7. X-ray Fluorescence

Both chloromethylated lignins were analyzed using XRF (X-ray Fluorescence). Using the Bruker EDX-XFlash 6/30 detector system at 7 kV. The concentrations were calculated using PB-ZAF standardless mode.

10.8. Calculation of Green Chemistry Metrics

With the goal of making chemistry a much greener field, a concrete set of metrics are required to analyze any given reaction and set certain standards in the field. The metrics described by Clark *et al* have been used for the following parameters: yield, conversion, selectivity, atom economy, reaction mass efficiency, optimum efficiency. The following zero passes were also used: solvents; health and safety; and critical elements.¹²

Anything above 89% in the yield, conversion and selectivity metrics is considered positive and anything below 70% is considered negative.

Table 2.1 Calculation of yield, conversion, and selectivity¹²

$$\text{Percentage yield} = \frac{\text{moles of product} \times 100\%}{\text{moles of limiting reactant}} \quad (1)$$

$$\text{Percentage conversion} = 100\% - \left(\frac{\text{final mass of limiting reagent} \times 100\%}{\text{initial mass of limiting reagent}} \right) \quad (2)$$

$$\text{Percentage selectivity} = \frac{\text{percentage yield} \times 100\%}{\text{percentage conversion}} \quad (3)$$

AE is a new metric that measures how many atoms from the reactants are represented in the final product, assuming 100% yield. This metric aids in analyzing how well the reaction is designed. RME focuses on the mass of the involved atoms instead and measures the observed values instead of the optimal. Comparing both gives a new metric of OE, which allows to compare reactions that can't have optimal AEs or RMEs.

Table 2.2 Calculation of atom economy, reaction mass efficiency, and optimum efficiency¹²

$$AE = \frac{\text{molecular weight of product} \times 100\%}{\text{total molecular weight of reactants}} \quad (4)$$

$$RME = \frac{\text{mass of isolated product} \times 100\%}{\text{total mass of reactants}} \quad (5)$$

$$OE = \frac{RME \times 100\%}{AE} \quad (6)$$

Another important factor in the green chemistry metrics of a reaction is the choice of solvent. There are solvents that are highly undesirable or hazardous and warrant an alternative. The article recommends the following: water, EtOH, *i*-PrOH, *n*-BuOH, EtOAc, *i*-PrOAc, *n*-BuOAc, anisole and sulfolane. There are also some recommended solvents that may be problematic: MeOH, *t*-BuOH, benzyl, alcohol ethylene glycol, acetone, MEK, MIBK, cyclohexanone, MeOAc, AcOH and Ac₂O.

The toxicity and potential hazards of the reactants are also important. The hazard codes from the globally harmonized system for classifying and labeling chemicals are used. In lack of an H-statement, caution should be exercised. The following hazard statements are undesirable: highly explosive (H200, H201, H202, H203), explosive thermal runaway (H240), fatally toxic (H300, H310, H330), may cause cancer (H350), repro-toxic (H360), serious environmental implications(H420).

The article brings another new metric into the discussion, which is sustainability that doesn't involve the carbon cycle. It considers the supply of all the elements and their known reserves. Elements with no given timeframe until depletions are the most desirable, then elements with a supply for 100-500 years. Shorter depletion times become problematic (50-100 years) and very problematic at 50-5 years.

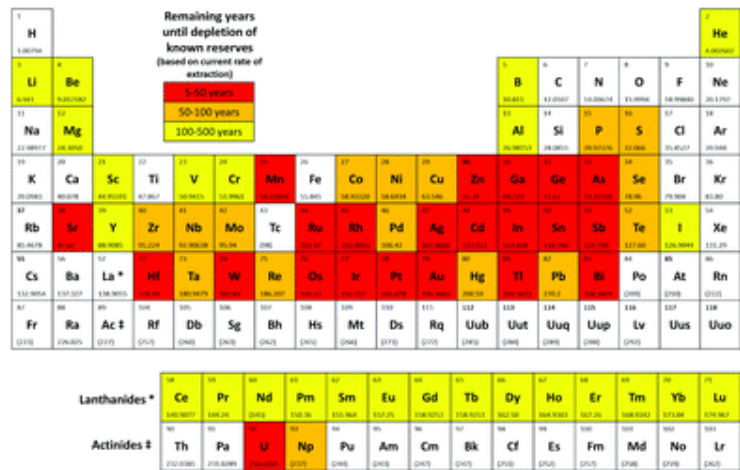


Figure 2.3 Periodic table showing critical elements¹²

11. Results and discussion

These results will focus on the chemical changes made to the lignin, as a complete understanding of the structure is not currently feasible.

11.1 NMR result for model compound and CML

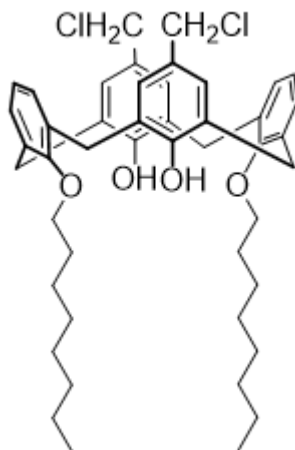


Figure 3.1 Structure of the chloromethylated model calix[4]arene

The ^1H NMR spectra of the chloromethylated 5,17-dioctyloxy-1,3-dihydroxycalix[4]arene (Figures 3.1 and 3.2) shows a triplet at 0.89 parts per million (ppm) which corresponds to the CH_3 group. The alkyl chain of the compound is shown from 1.26 to 2.05 ppm. The doublet at 3.28 and 4.29 ppm corresponding to the axial and equatorial protons of the methylene bridge connecting the aromatic fragments. The triplet between the doubles corresponds to the methylene fragment bound with oxygen. The most important signal is at 4.51 ppm, it is the characteristic peak for chloromethylated calixarenes, which confirms that chloromethylation did take place. From 6-9 ppm all the aromatic fragments are depicted. There are two groups of aromatic rings, the first one has a triplet at 6.77 ppm and a doublet at 6.93. The peak at 7.08 corresponds to a ring that has a chloromethyl group. The remaining peak at 8.44 corresponds to free hydroxyl groups.

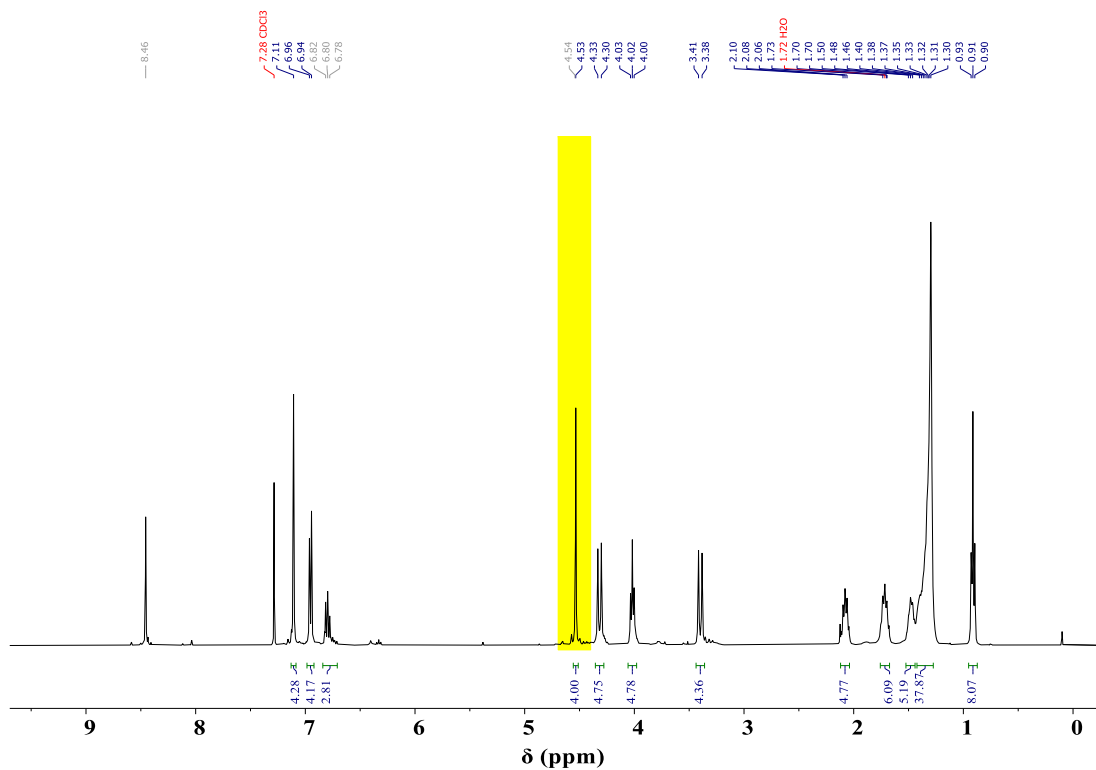


Figure 3.2 ^1H NMR spectra of the chloromethylated model calix[4]arene

Similarly, a new peak at 4.5-4.6 ppm was observed (**Figure 3.3**) in the case of chloromethylated lignin confirms that the successful chloromethylation on the phenolic rings. Additionally, NMR findings confirm that the chemical modification did not disturb the lignin's polymeric structure.

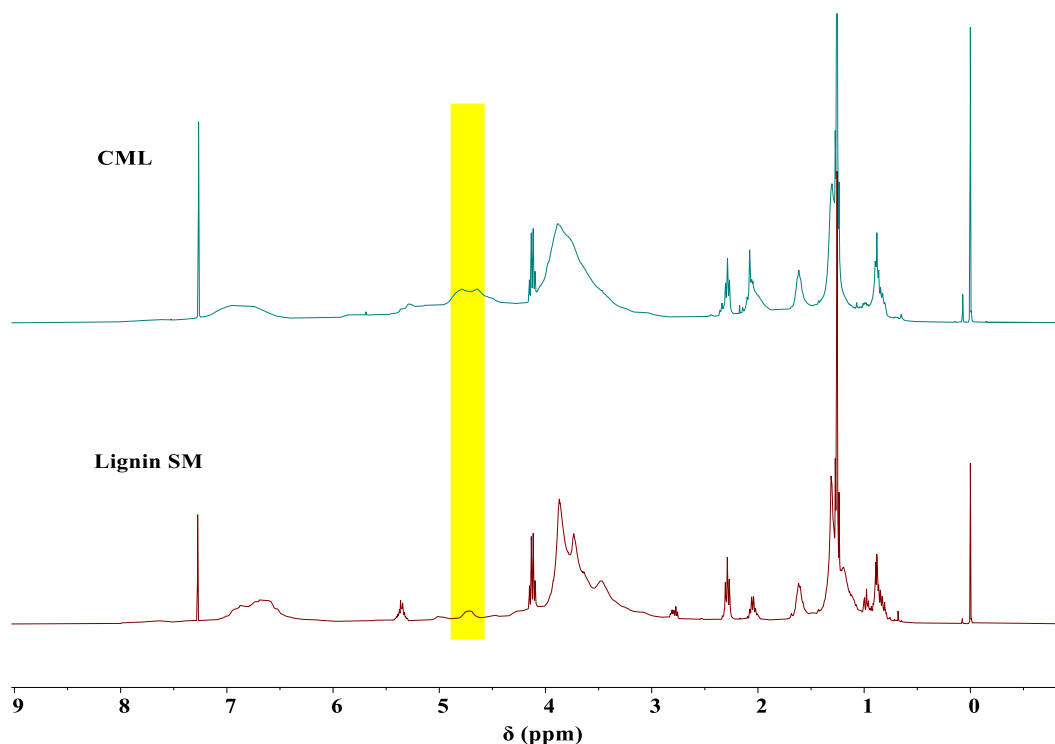


Figure 3.3 ^1H NMR spectra of the chloromethylated lignin compared with Lignin starting material

11.2 XRF results for both chloromethylated products

The XRF method revealed that the chloromethylated lignin using the newer method contained 20.0% chlorine and the one using titanium chloride contained 1.2% chlorine.

11.3 Green Chemistry Metrics

Simplification was required due to the random nature of the lignin polymer. The average molecular mass of the monolignols were used in the calculations (Figure 2.2).

Method	Yield	Conversion	Selectivity	AE	RME		OE
CML1	20	20	99.9	92.5	12.7		13.7
CML2 - TiCl_4	1.2	1.5	78.9	61.7	0.8		1.2

Table 3.1 Green Chemistry metrics for the two methods of chloromethylation of lignin

The new reaction using formaldehyde and acidic acid has a much higher yield and conversion than the TiCl_4 reaction. For green chemistry metrics the value of even the newer reaction is considered very low, but it is a large improvement considering the 90%+ selectivity, which by the green chemistry metrics is a great result and should be explored further. The reaction using titanium has a selectivity under 80% which is very undesirable, as it means reagents are wasted on side reactions. The AE of CML1 is 92.5%, which shows that the reaction is well designed, as most of the atoms used in it are

represented in the final product. CML2 has its AE % at a much lower value of 61.7%, which means that almost half of the atoms used in the reaction do not make it into the final product and are wasted unless they can be recovered.

The low RMI values for CML1 and CML2 come from their low yield and conversion, where the mass of the unreacted and/or side reaction products outweigh the mass of the product heavily. CML1-s is higher due to a higher yield and conversion rate. The most important part of the OE, how close it is to an ideal green chemistry reaction. CML1 is 13.7% of its optimum efficiency, which is promising, considering CML2 has it at a low 1.2%.

The CML1 method uses reagents that are not under risk of running out in the next 100-500 years, and used solvents from the recommended list, water, and acetic acid. Originally methanol was used to filter the product but was replaced with a solution of acetic acid due to its innate toxicity.

The CML2 method uses titanium, which is at risk of running out in the next 5-50 years and would not be sustainable by current estimations. It also uses problematic solvents like chloroform and CH_2Cl_2 . Another important note is the energetic cost required to run this reaction, as it requires low temperatures.

11.4 Potential uses of new polymer

Chlorinated polymers are used to make films of paint or varnish due to their properties. They are highly resistant to atmospheric effects, they have low biodegradability, they are highly soluble in organic solvents, and they adhere strongly to metals and porous materials. If these properties are retained within the lignin, it could be used to manufacture such paints or varnishes.

In the original paper where the alternate chloromethylation reaction was found, it contained a reaction pathway to synthesize a catalyst for the Suzuki cross coupling reaction¹⁴, which is one of the most important organic chemistry reactions. This new chloromethylated lignin could be used as a scaffold to create many of these catalytic centers for this reaction.

Another way to utilize this polymer is to create a quaternary ammonium salts out of the chlorine groups. These salts interact with the bacterial membrane after the hydrophobic tail is integrated. This denatures structural proteins and enzymes, damaging the membrane and ultimately killing the bacteria.¹⁹ This coating could then be applied wherever needed and disrupt any microbial life that comes into contact with it.

12. Conclusion

Lignin is the second most abundant biopolymer in the world and is part of the cell wall structure of plants from the vascular phyla. Being part of cell wall alongside cellulose and hemicellulose, it produced in large numbers from the wood pulping industry. Unlike cellulose, lignin is heavily underutilized, mostly being burned as low-grade fuel.

To aid in utilizing this abundant resource, new reactions are required, reactions that are also environmentally friendly. A promising new potential chloromethylation reaction has been found in search of this goal. This is an important step for the future valorization of lignin. The addition of the chloromethyl group allows many new possible reactions for valorization and easier modification of the polymer.

All the set goals were achieved. The model compound proved to be a good analogue for lignin. A new type of lignin was synthesized. The new reaction had a 16 times larger yield and was very selective. The lignin was analyzed using XRF and its green metrics were calculated and found to be much better than an alternative reaction.

The reaction's conversion and yield could be improved to minimize the number of unreacted molecules in the synthesis, in the future. Most importantly new potential reactions should be sought out with this polymer and tested.

13. Acknowledgements

I would like to thank my instructor Yevgen Karipchev for their help both in the lab and in writing this thesis. I would also like to thank Mahendra K. Mohan and for his continued work on this reaction and help in writing and improvement of this thesis work. I would also like to give a special thanks to Oleg Silenko, PhD who helped me to explore the world of calix[4]arenes, providing the model compound and helping me at every step in the lab. I would also like to thank the whole wood chemistry department for their amazing work with a compound as stubborn as lignin.

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15. Appendix

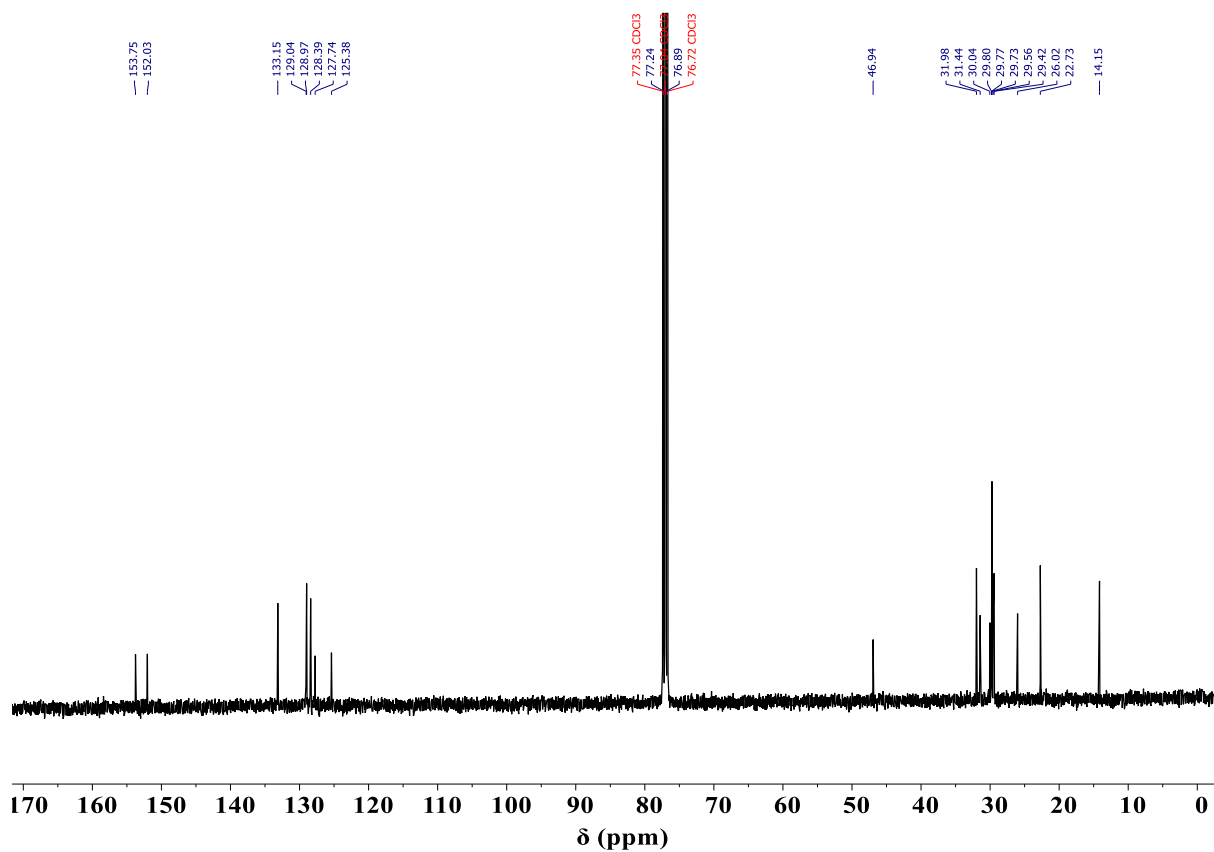


Figure A1. ^{13}C NMR spectra of the chloromethylated calix[4]arene.

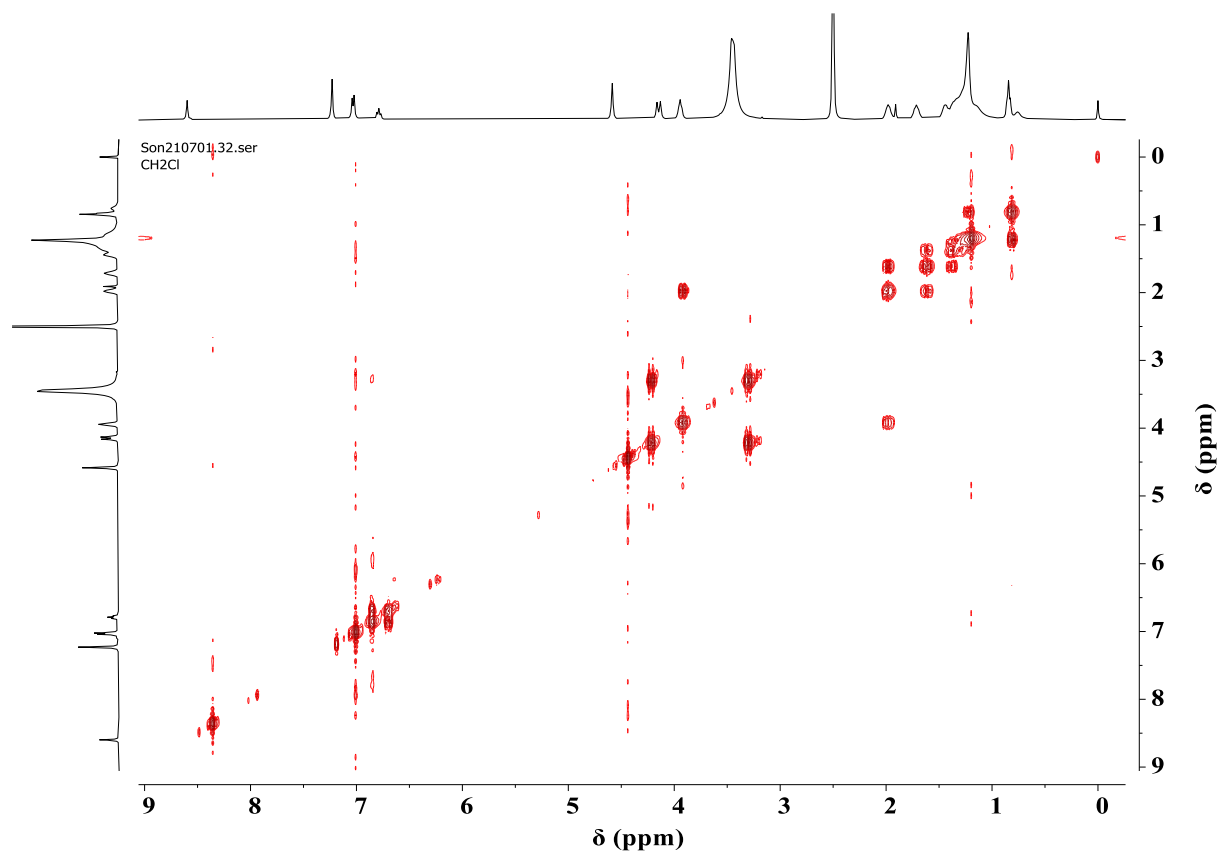


Figure A2. HSQC spectra of the calix[4]arene.

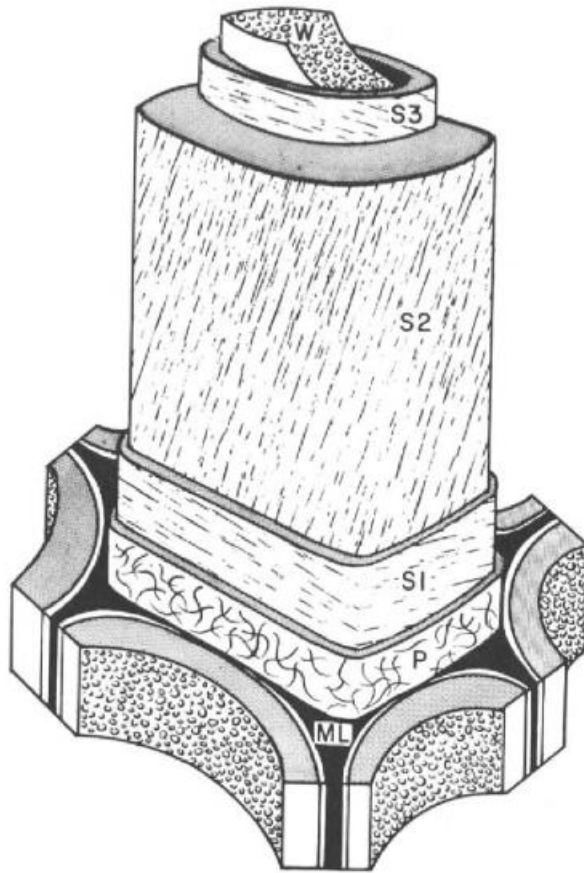


Figure A3. Simplified structure of a woody cell. Where ML is the middle lamella, P the primary wall, S1 the outer secondary wall, S2 the middle secondary wall, S3 the inner secondary wall, and W the watery layer ⁴

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