Application of Lignin NMR Techniques For Wood Extractives

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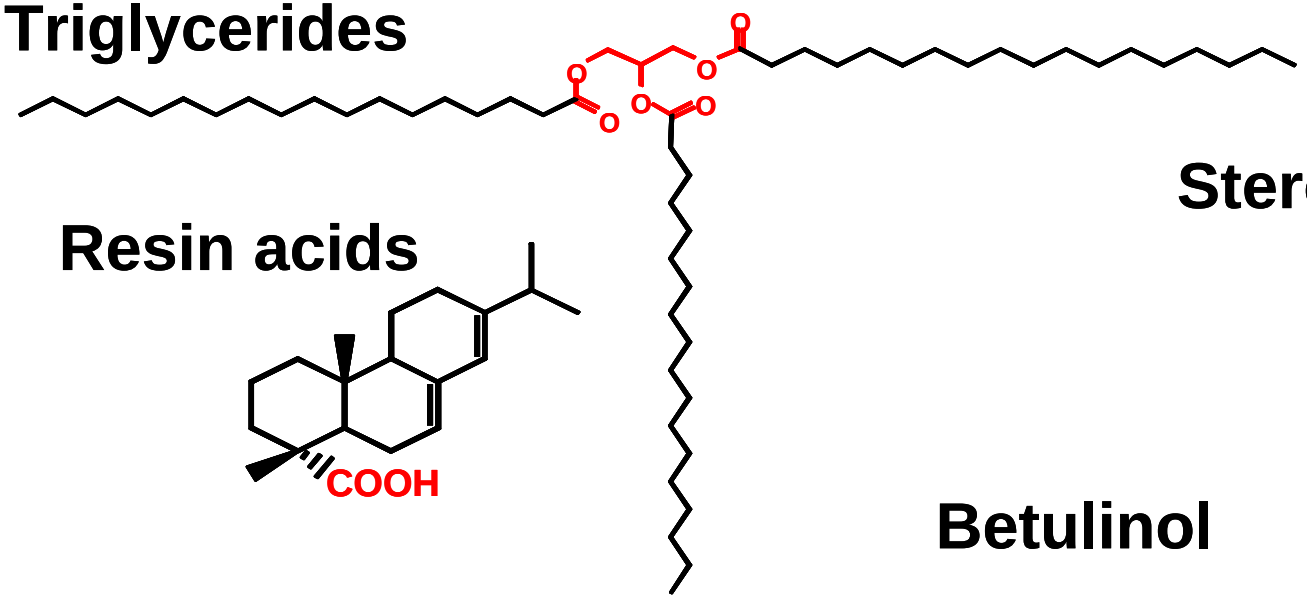
Aim

- Follow-up to recent report on role of extractives in contaminating isolated residual lignins samples and analysis?

- Can lignin NMR techniques be used to analyze/ characterize wood extractives?

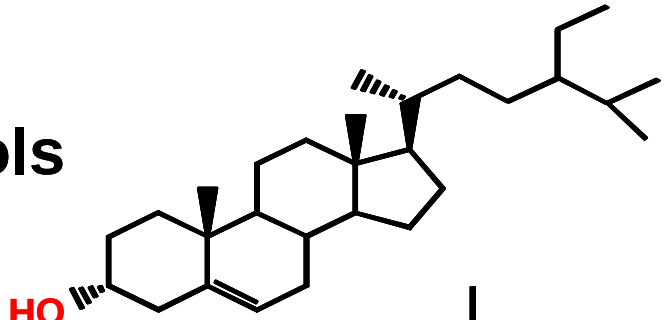
Wood Extractives

Triglycerides

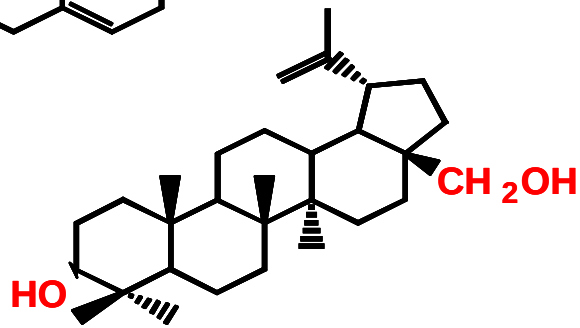


Resin acids

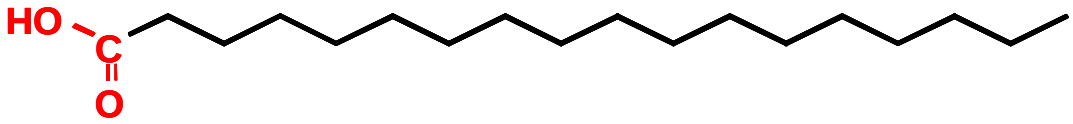
Sterols



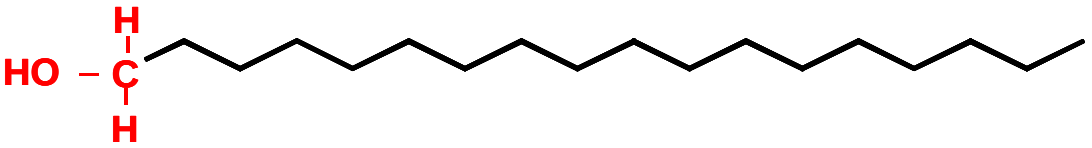
Betulinol



Fatty acids



Fatty alcohols



Alkanes

Wood Extractives

- Has something been overlooked?
- Non-extractable wood extractives?
- Lignin-Extractives-Complexes, LEC
- ^{1}H, ^{13}C, ^{31}P NMR
- Py-GC/MS and TOF-SIMS

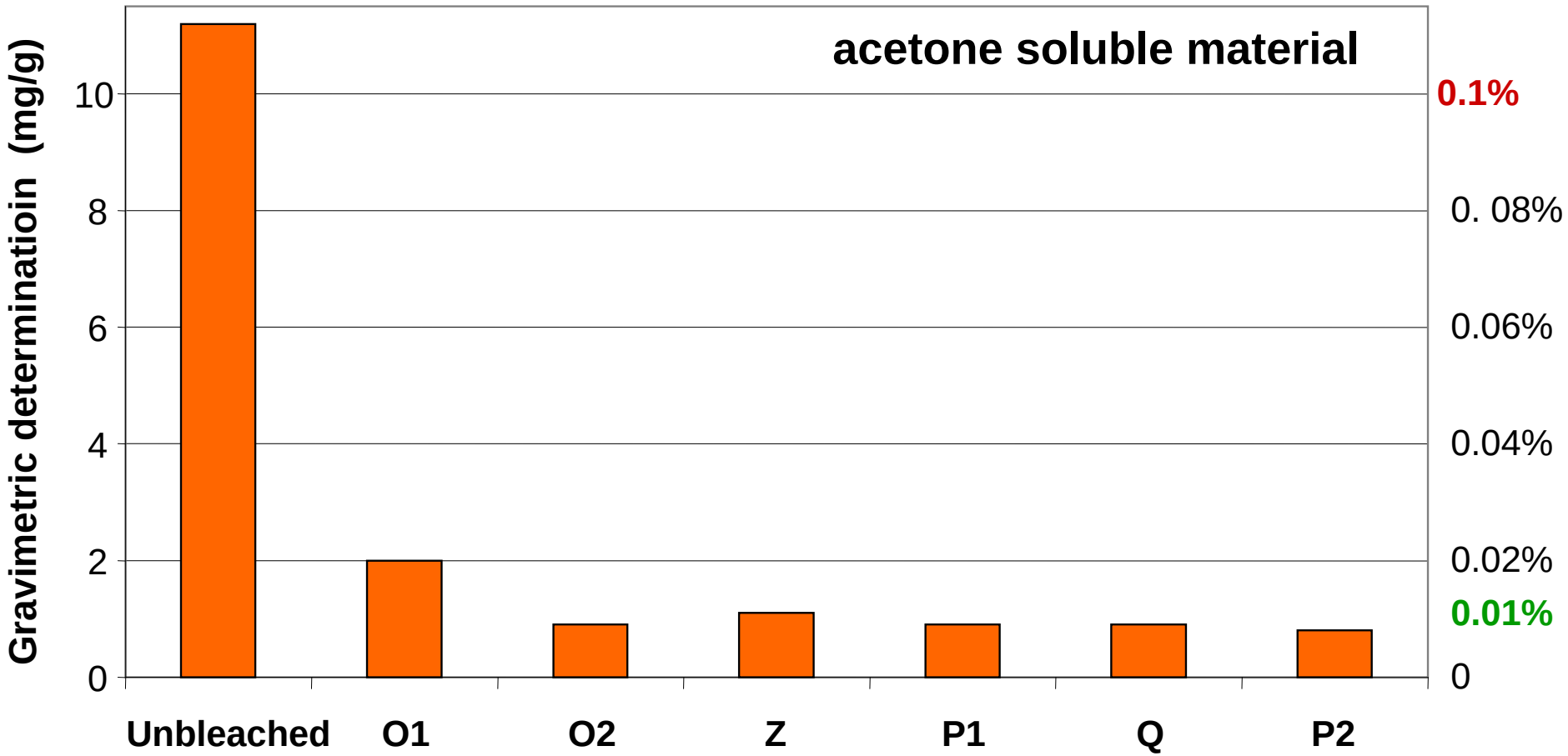
Extraction of Pulp

Soxhlet

SoxTec

ASE
(Accelerated
Solvent Extractor)

Amount of Wood Extractives in Pulps from a SW Kraft Mill



Wood Extractives in Fractionated Pulps

	O1			O2			Z			P1			Q			P2			labP2	
	pul	**fin**	**fib**	**pul**	**fin**	**fib**	**pul**	**fin**	**fib**	**pul**	**fin**	**fib**	**pul**	**fin**	**fib**	**pul**	**fin**	**fib**	**fin**	**fib**
Sum	135	**672**	15	42	**418**	11	27	**186**	13	17	**159**	14	25	**85**	8	11	**76**	13	**195**	7

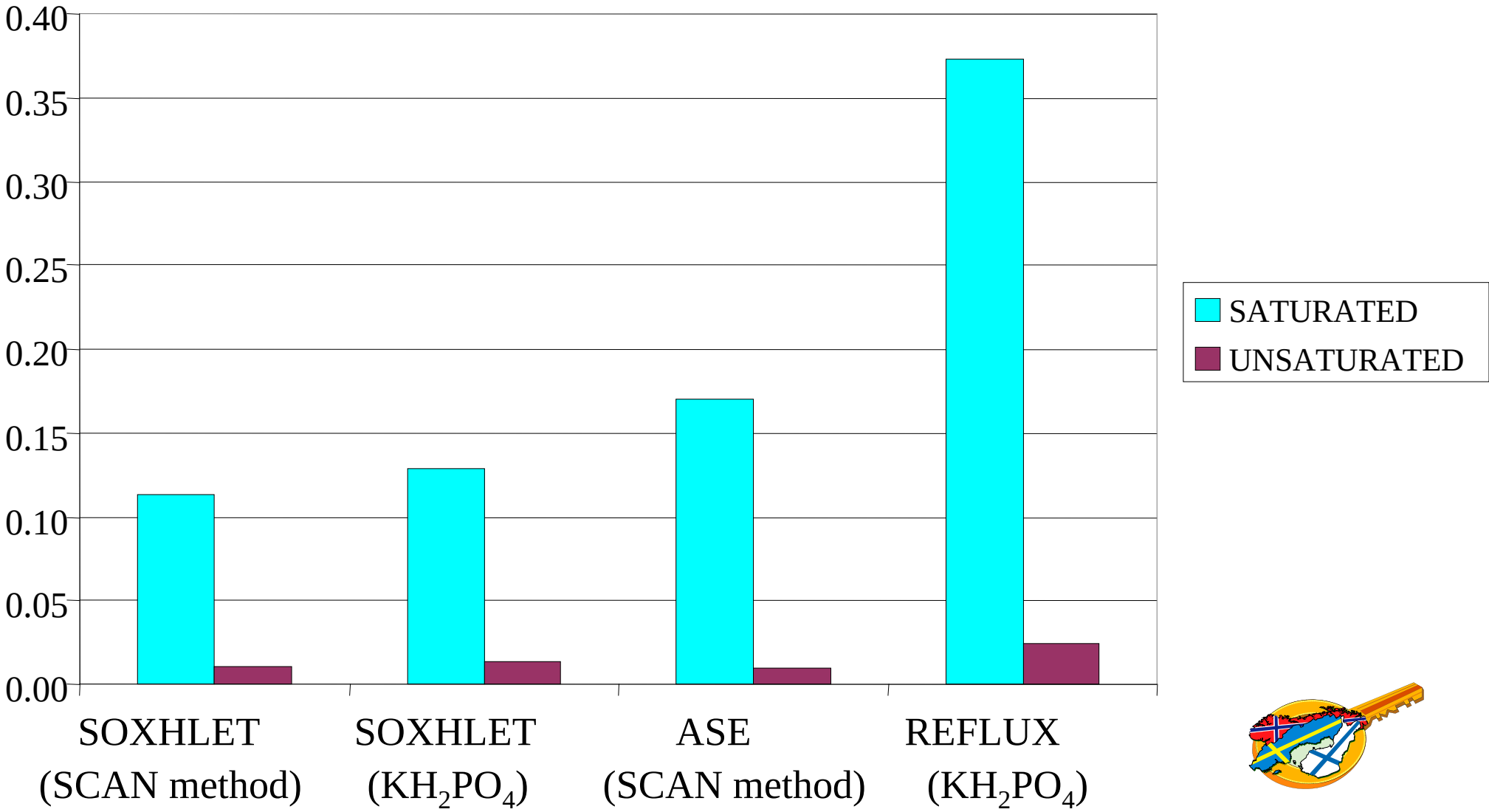
(microgram/gram)

Most of the wood extractives are present in the fines fraction

Laine, Tamminen and Nilvebrant EWLP 2000

FATTY ACIDS IN A BLEACHED PULP

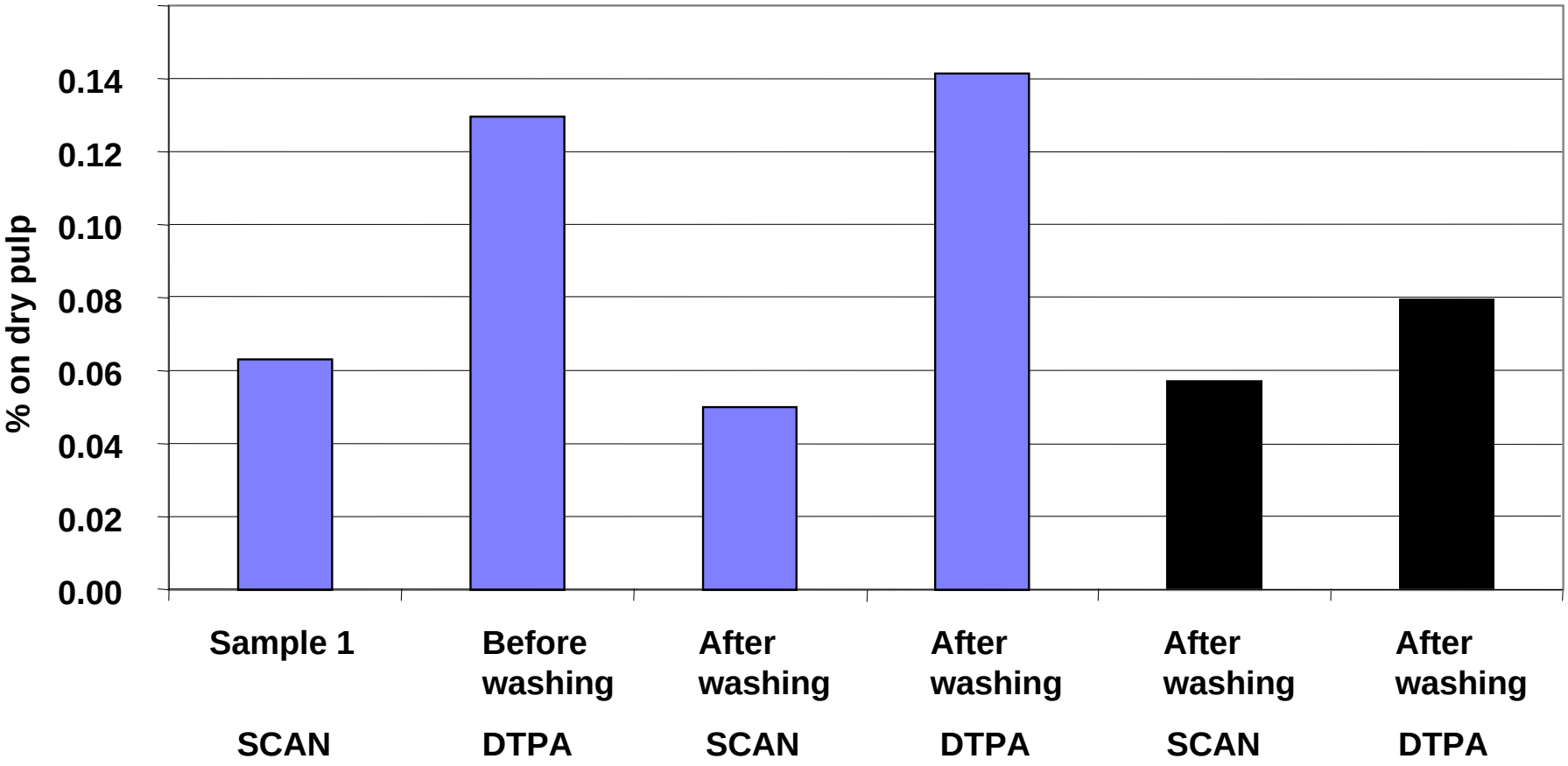
different extraction methods



From Holmbom et al 2001

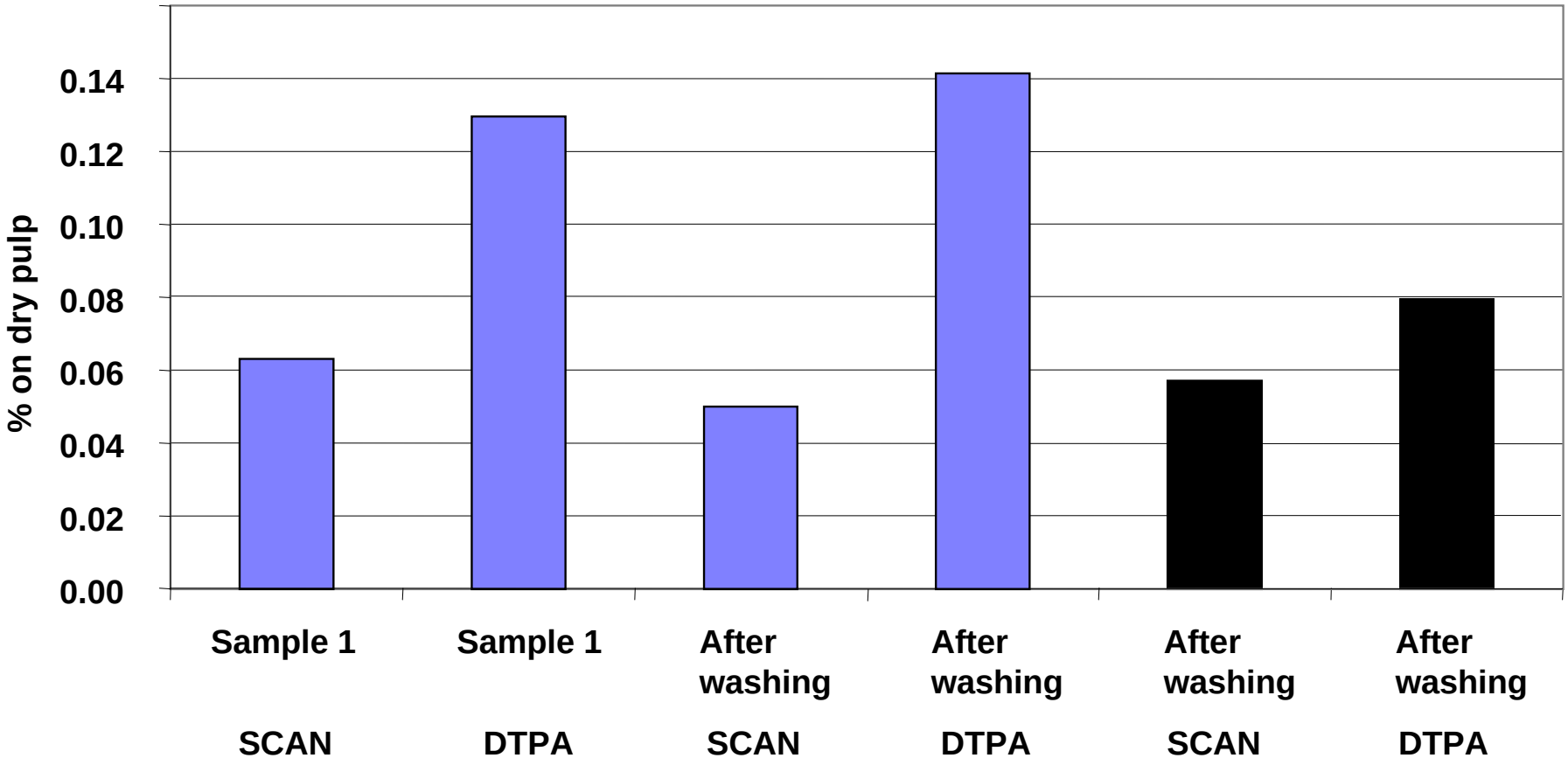
Incomplete Extraction of Extractives

Amount of wood extractives in an unbleached SW kraft pulp



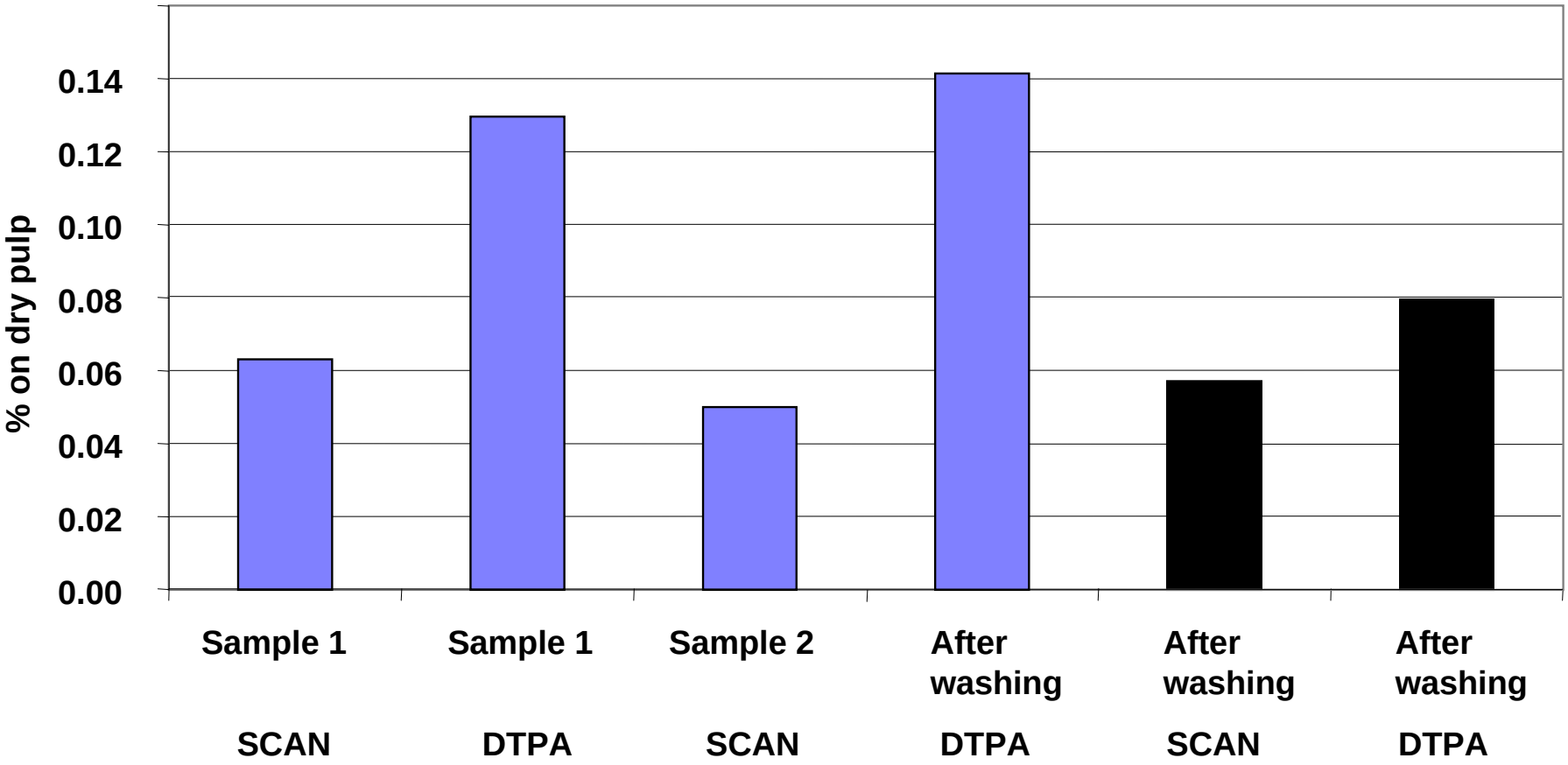
Incomplete Extraction of Extractives

Amount of wood extractives in an unbleached SW kraft pulp



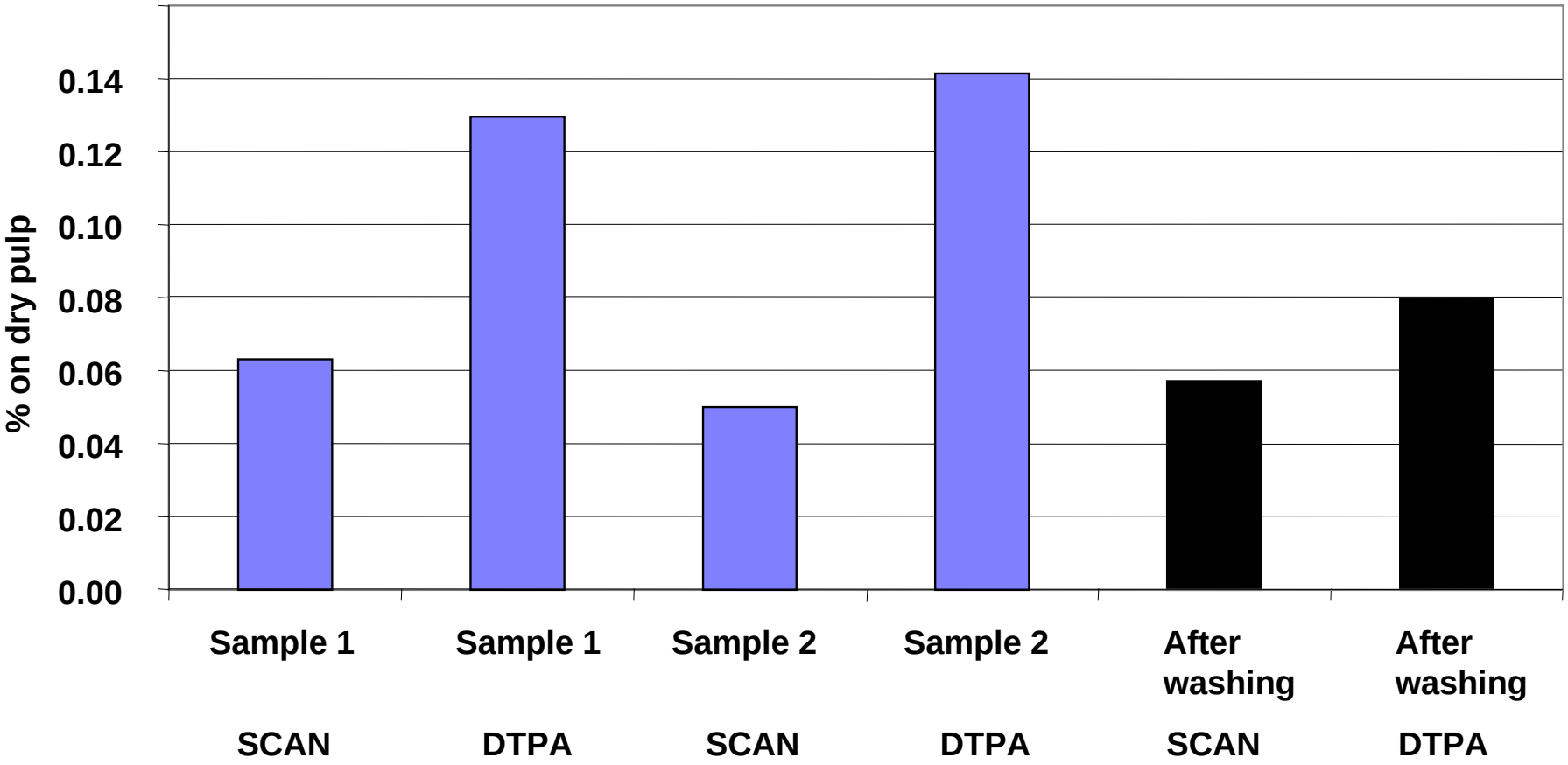
Incomplete Extraction of Extractives

Amount of wood extractives in an unbleached SW kraft pulp



Incomplete Extraction of Extractives

Amount of wood extractives in an unbleached SW kraft pulp

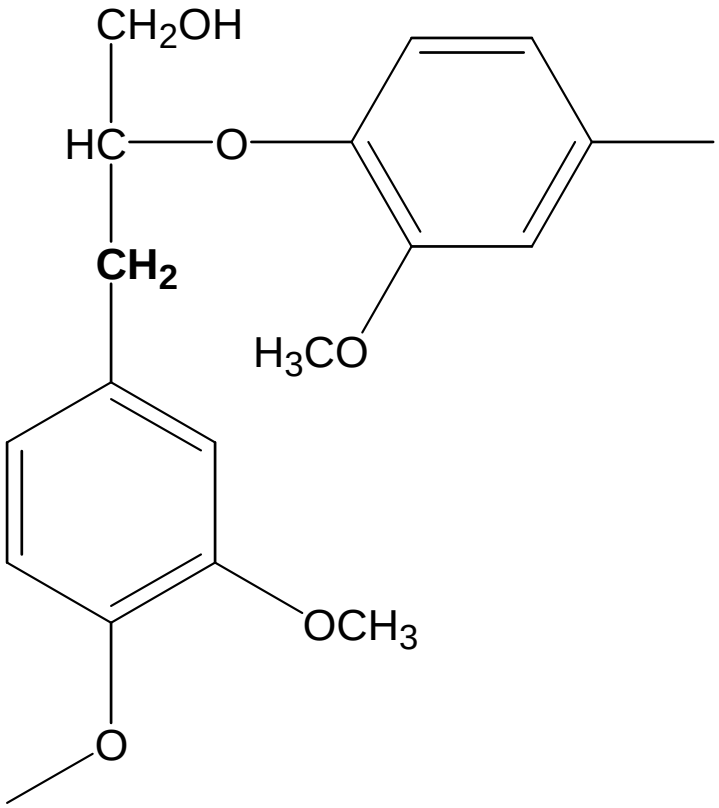


It has been concluded that residual lignins;

- contain unreactive aliphatic CH_x-structures
- CH_x-structures are present as reduced hydrocarbon groups after the cook
- carbohydrates are linked in Lignin-Carbohydrate-Complexes LCC
- all wood extractives may be removed by solvent extraction

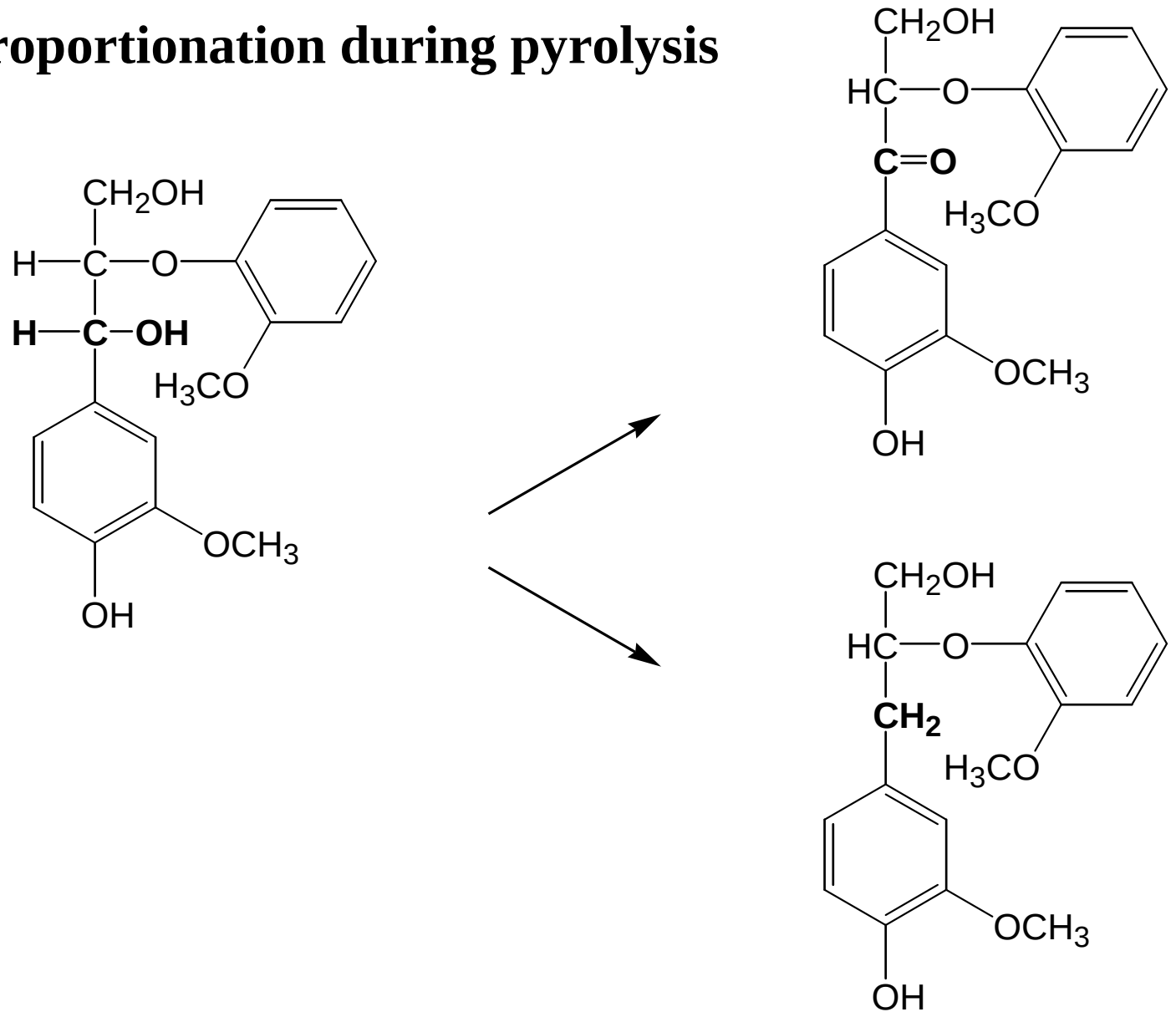
How sure can we be that there do not exist Lignin-Extractives-Complexes, LEC ?

Reduced Structures in Isolated Lignins

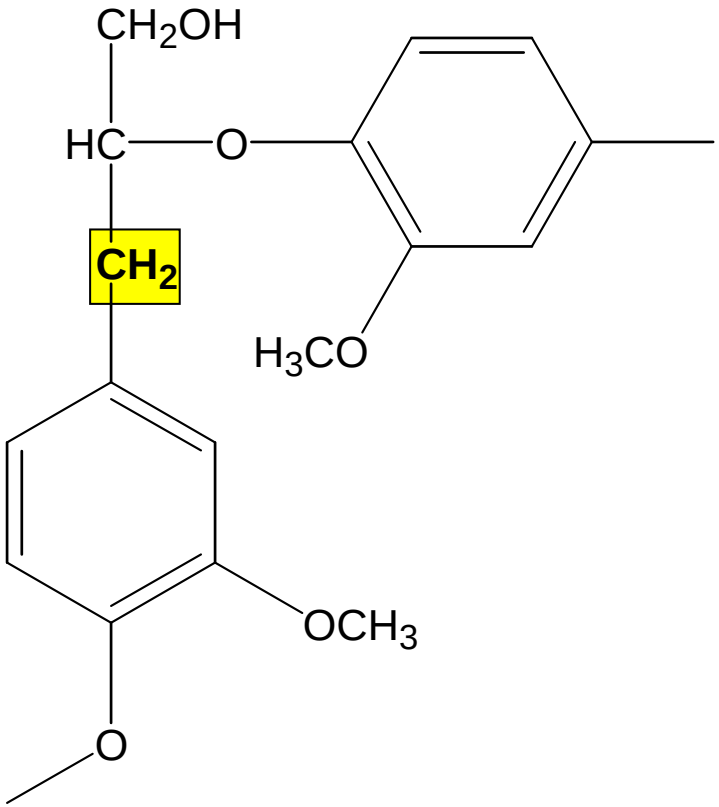


Do such exist?

Disproportionation during pyrolysis



Reduced, α-CH_2, Structures in Lignins



or traces of

CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-COOH

Isolation of Residual Lignin From Pulps

- **Acidic degradation of carbohydrates**
- **Enzymatic degradation of carbohydrates**
- **Combined degradations of carbohydrates**

Isolation of residual lignins from SW and HW pulp

Unbleached kraft pulp

↓ Extraction of pulp with 1) acetone and 2) DCM

↓ Acidic aqueous dioxane hydrolysis

Residual lignin from pulp

↓ Pentane-extraction

“Extractive-free” residual lignin

Extraction of Pulps

Acidify **Before or during extraction**

- **Alkaline process conditions leads to the formation of salts**
- **Fatty acids form insoluble i.e. calcium soaps**
- **Saturated fatty acids trapped in the pulp**
- **DTPA or phosphate have to used**

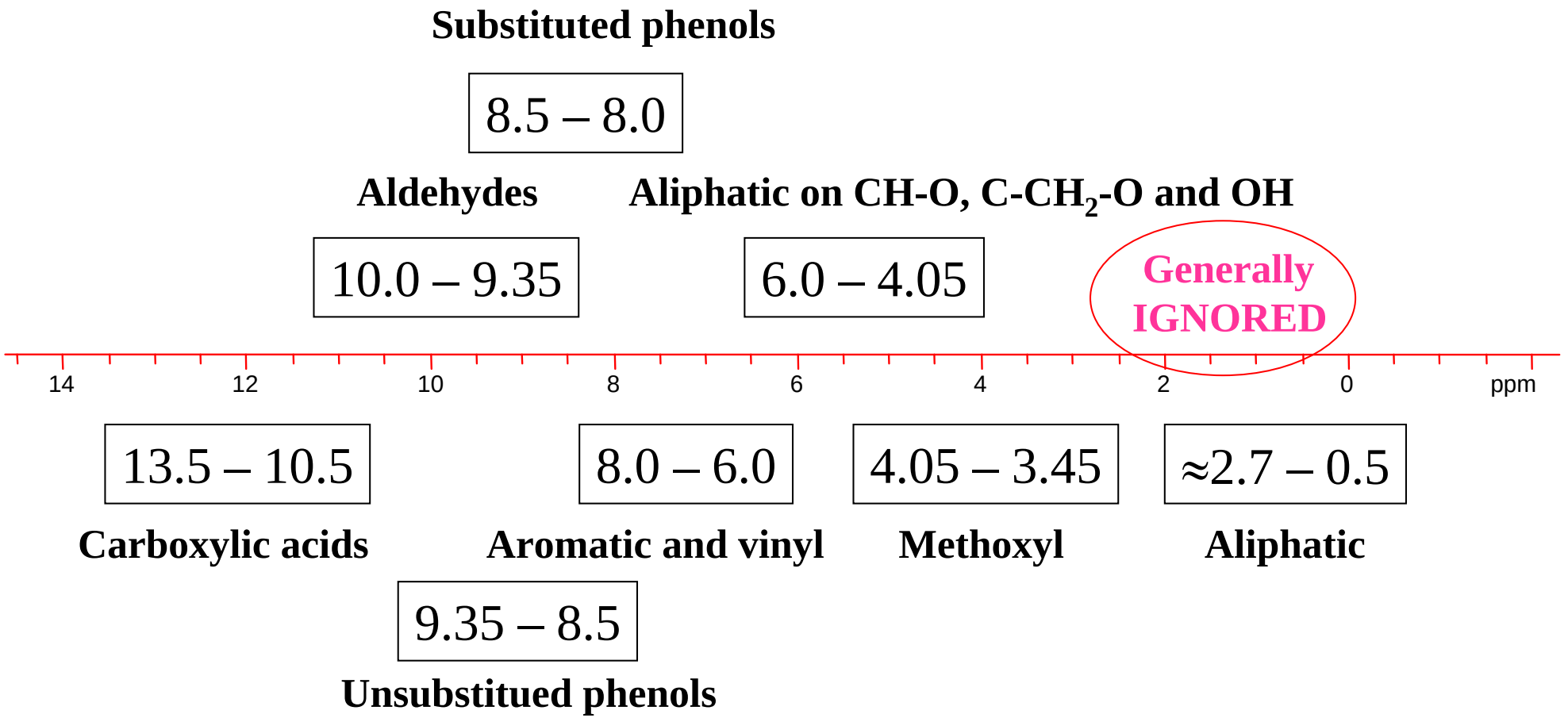
Dry before extraction

- **Air-drying may lead to oxidation of linoleic acid and betulaprenols**
- **Freeze- drying is preferred**

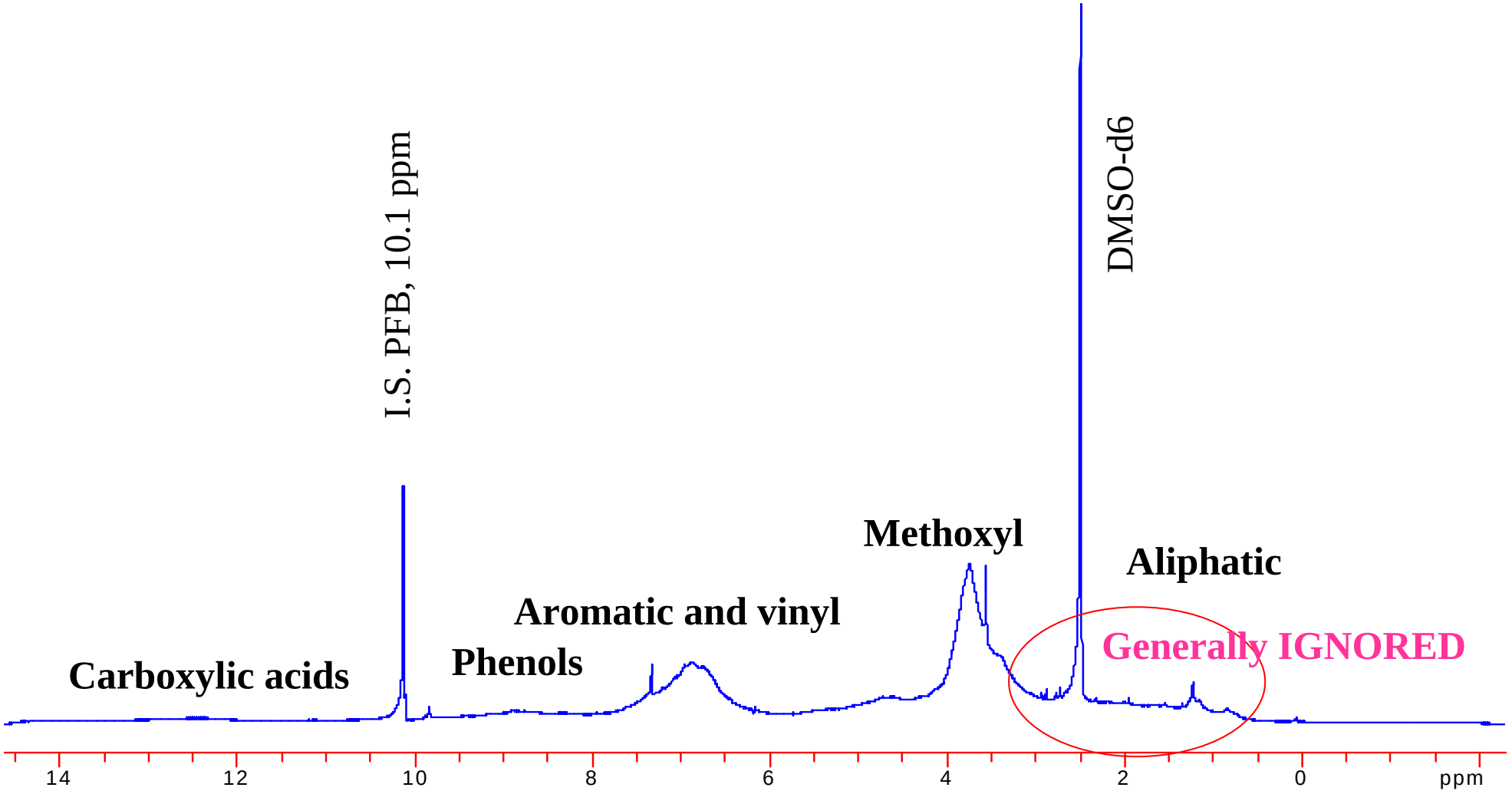
Holmbom et al 2001

^{1}H NMR

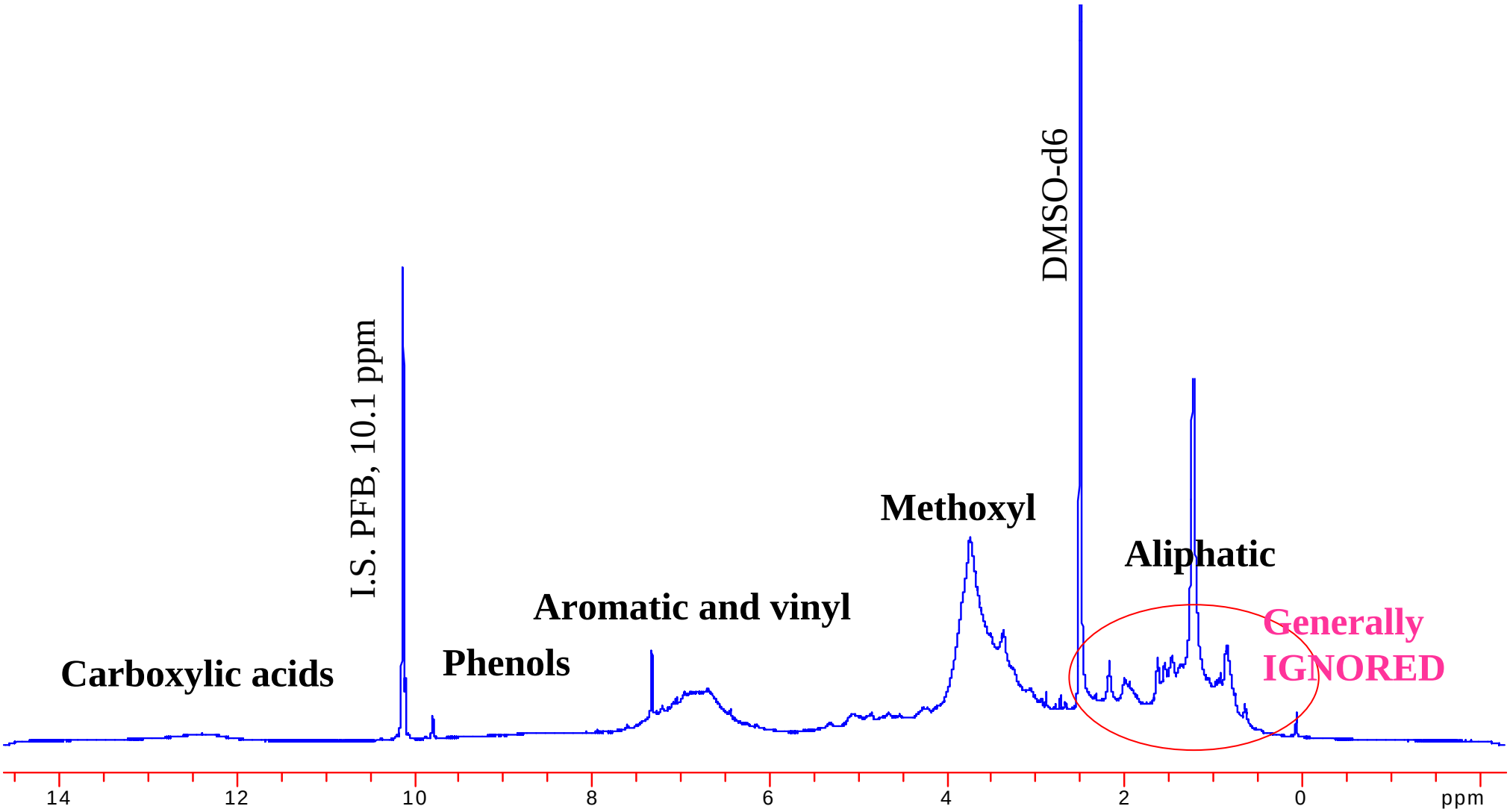
Chemical shifts



^{1}H spectrum of isolated lignin from unbleached SW kraft pulp



^{1}H spectrum of isolated lignin from unbleached HW kraft pulp



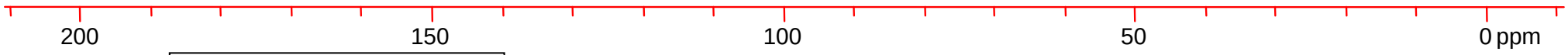
^{13}C NMR

Chemical shifts

Carboxylic acid, unconjugated

178.0 – 167.5

29.9 – 27.0

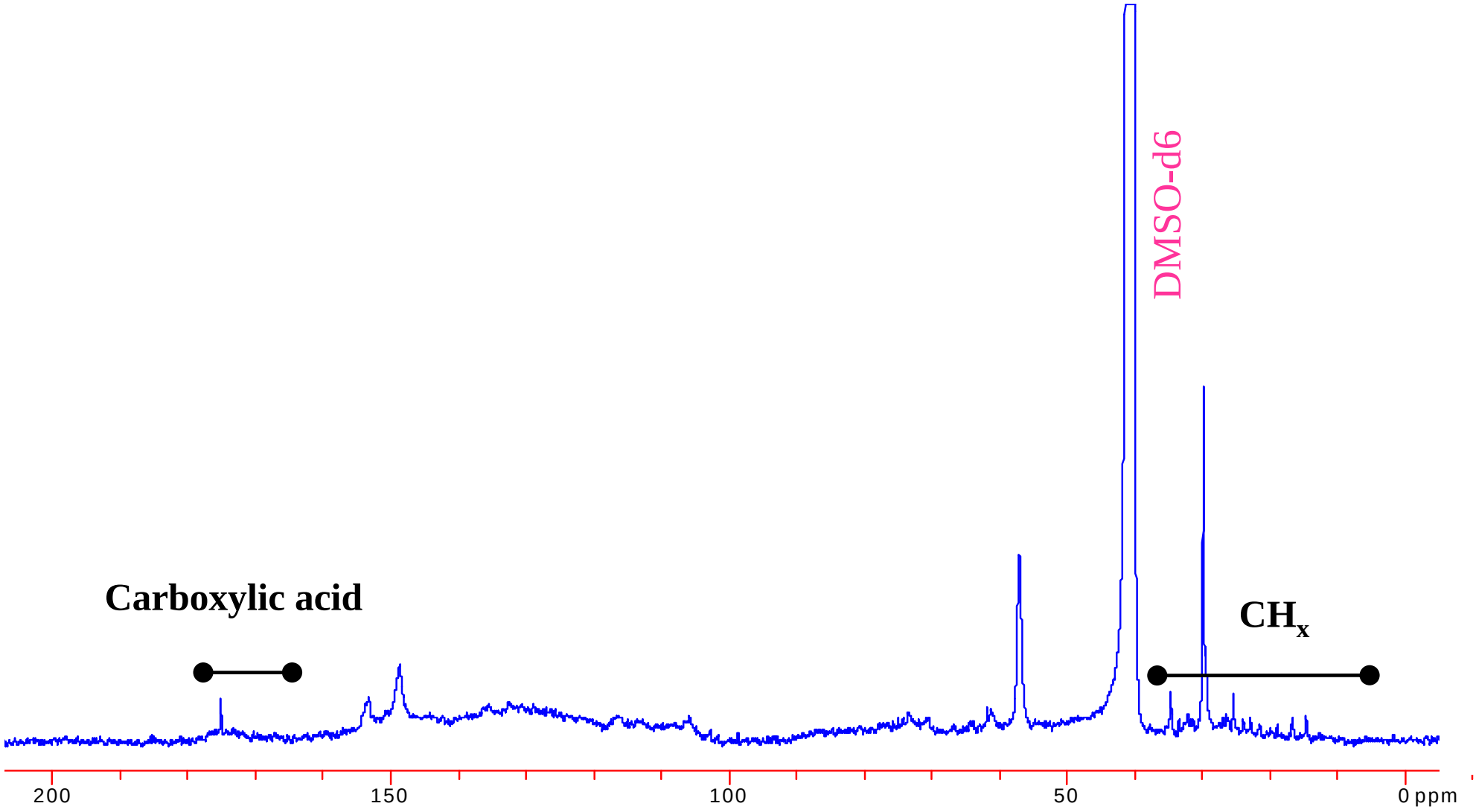


167.5 – 162.5

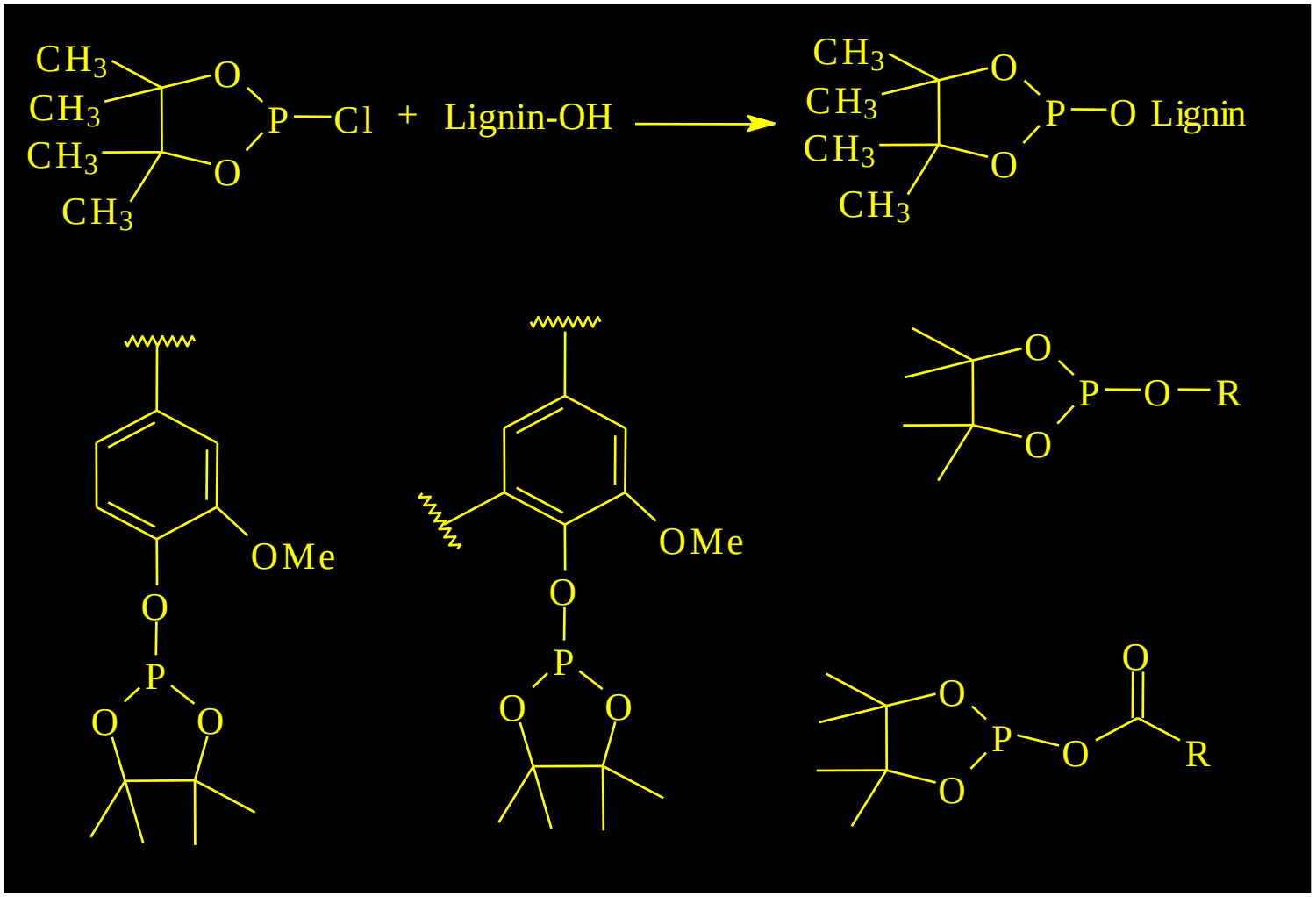
CH_2 in diaryl methane

Carboxylic acid, conjugated

^{13}C NMR of isolated lignin from unbleached HW kraft pulp



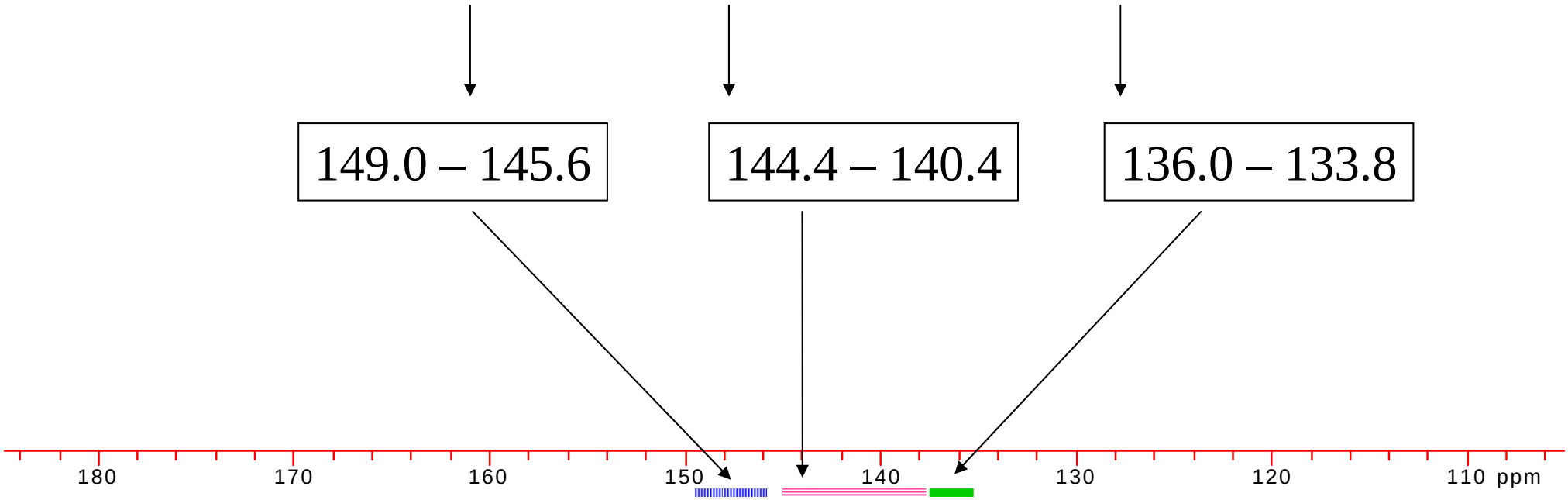
Characterization of Residual Lignins
^{31}P NMR



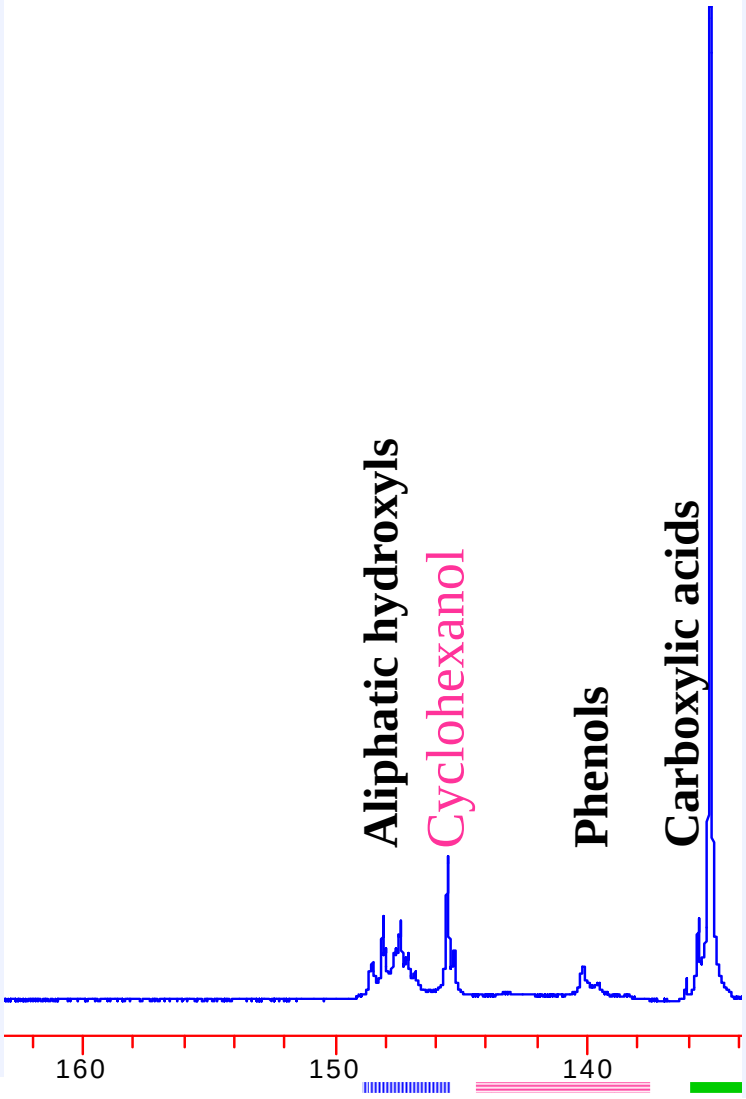
^{31}P NMR

Chemical shifts

aliphatic hydroxyl groups, **phenols** and **carboxylic acids** in softwood lignins



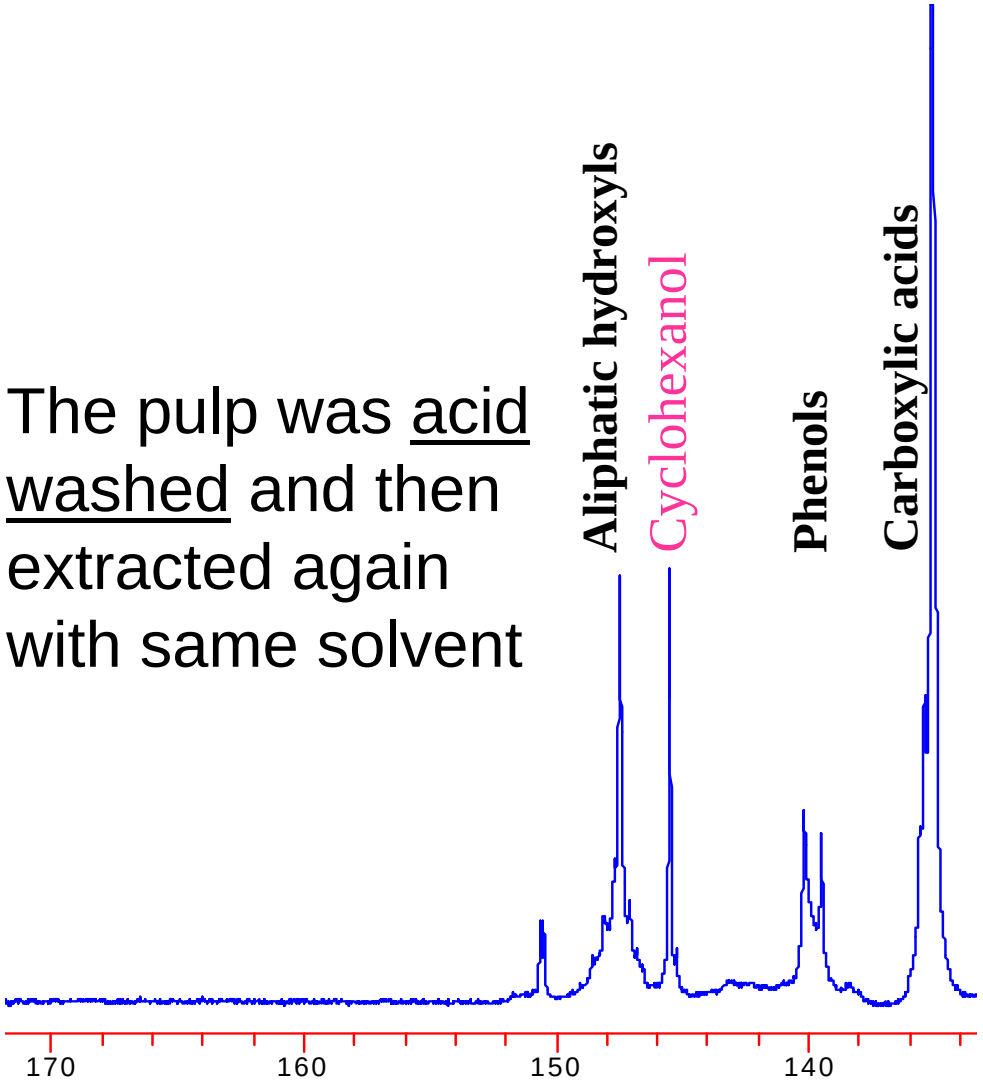
^{31}P NMR Extract from a SW Pulp



^{31}P NMR Extract from a SW pulp the same pulp

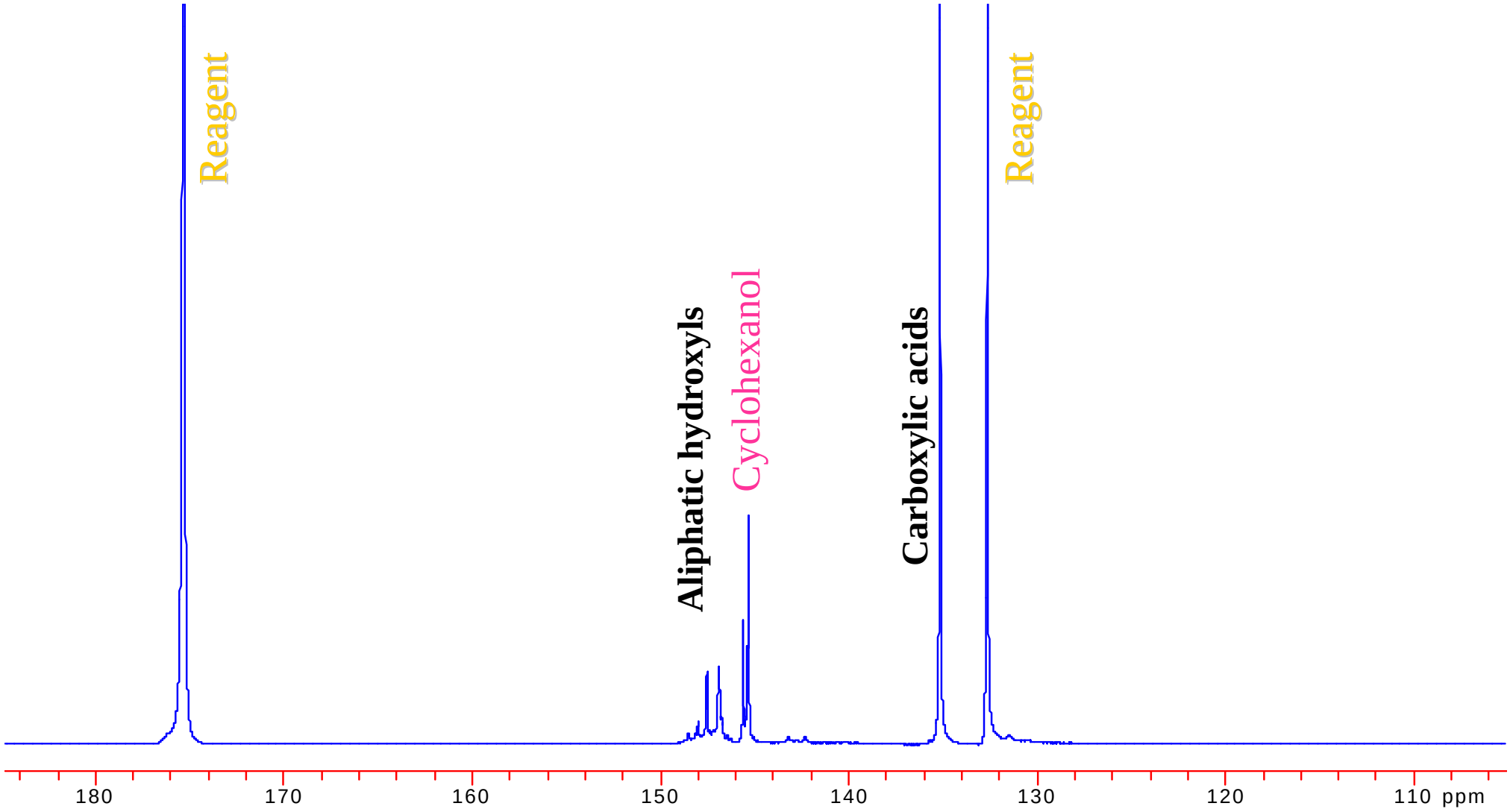
Isolated from an "already-extracted" pulp

The pulp was acid washed and then extracted again with same solvent



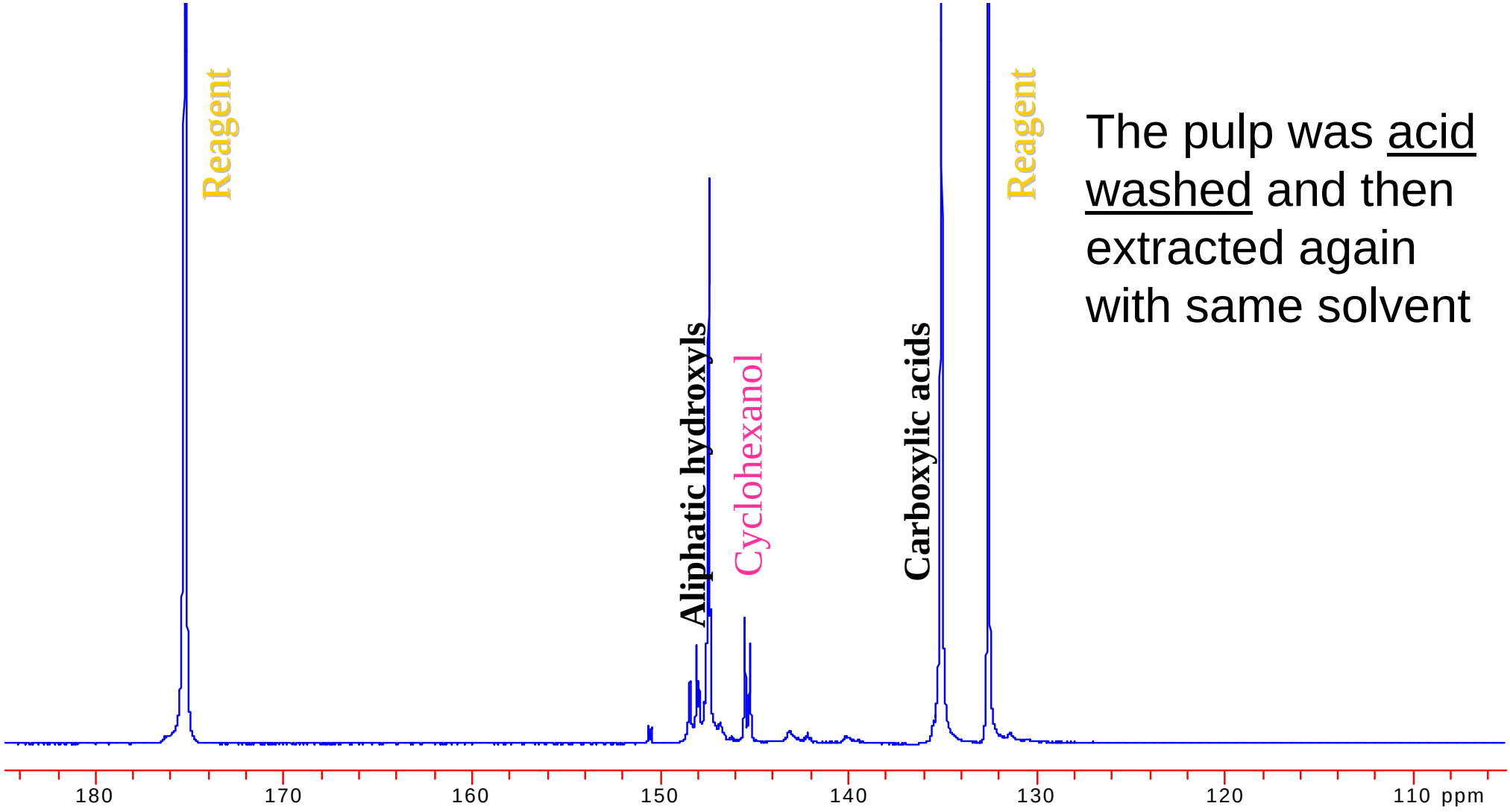
This is a softwood extractive sample that was isolated from an "already-extracted" pulp. The pulp was acid washed and then extracted again with methylene chloride (same solvent used as when first extracted) to obtain the sample.

^{31}P NMR of extractive sample from hardwood pulp



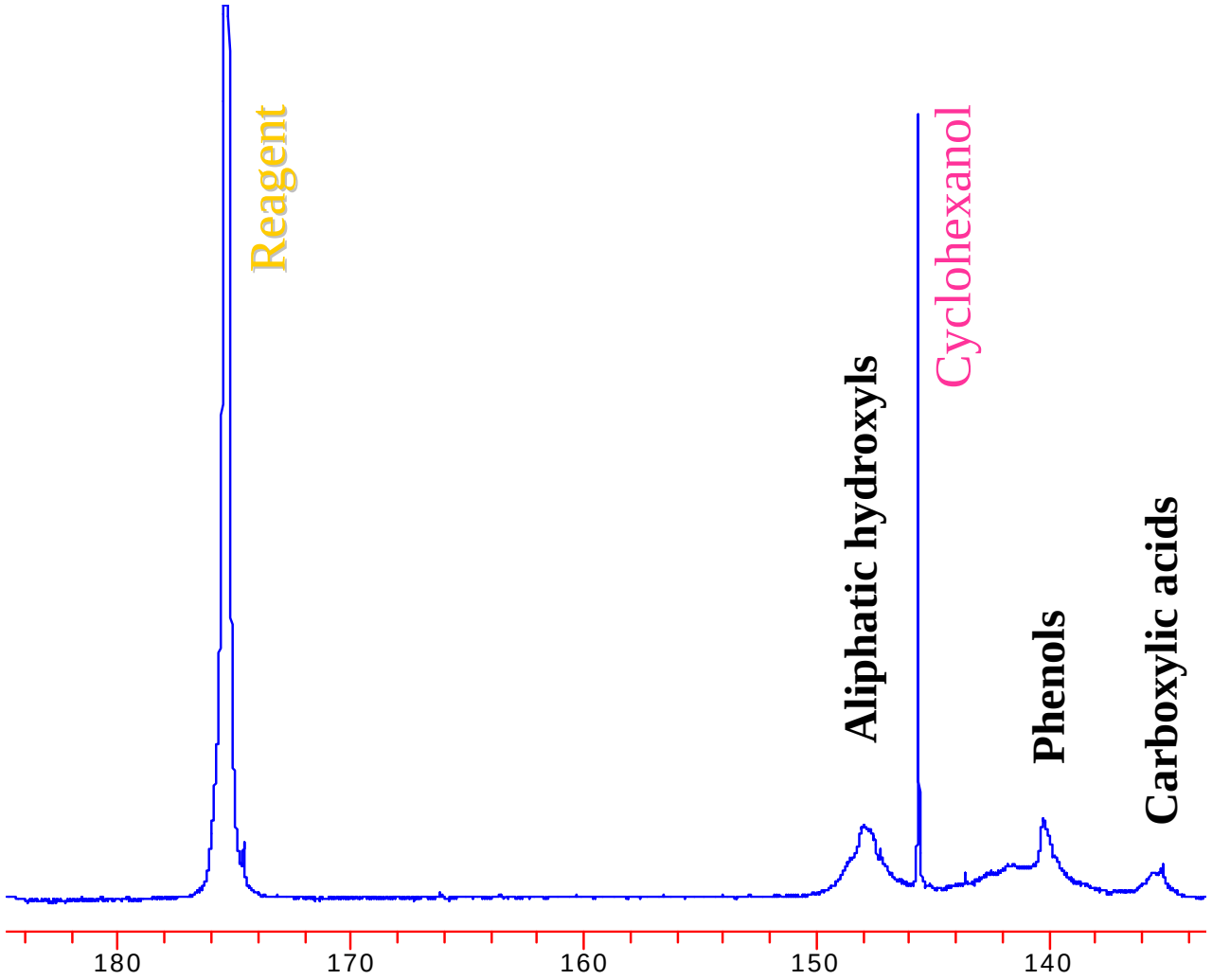
^{31}P NMR of extractive sample from hardwood pulp

Isolated from an "already-extracted" pulp

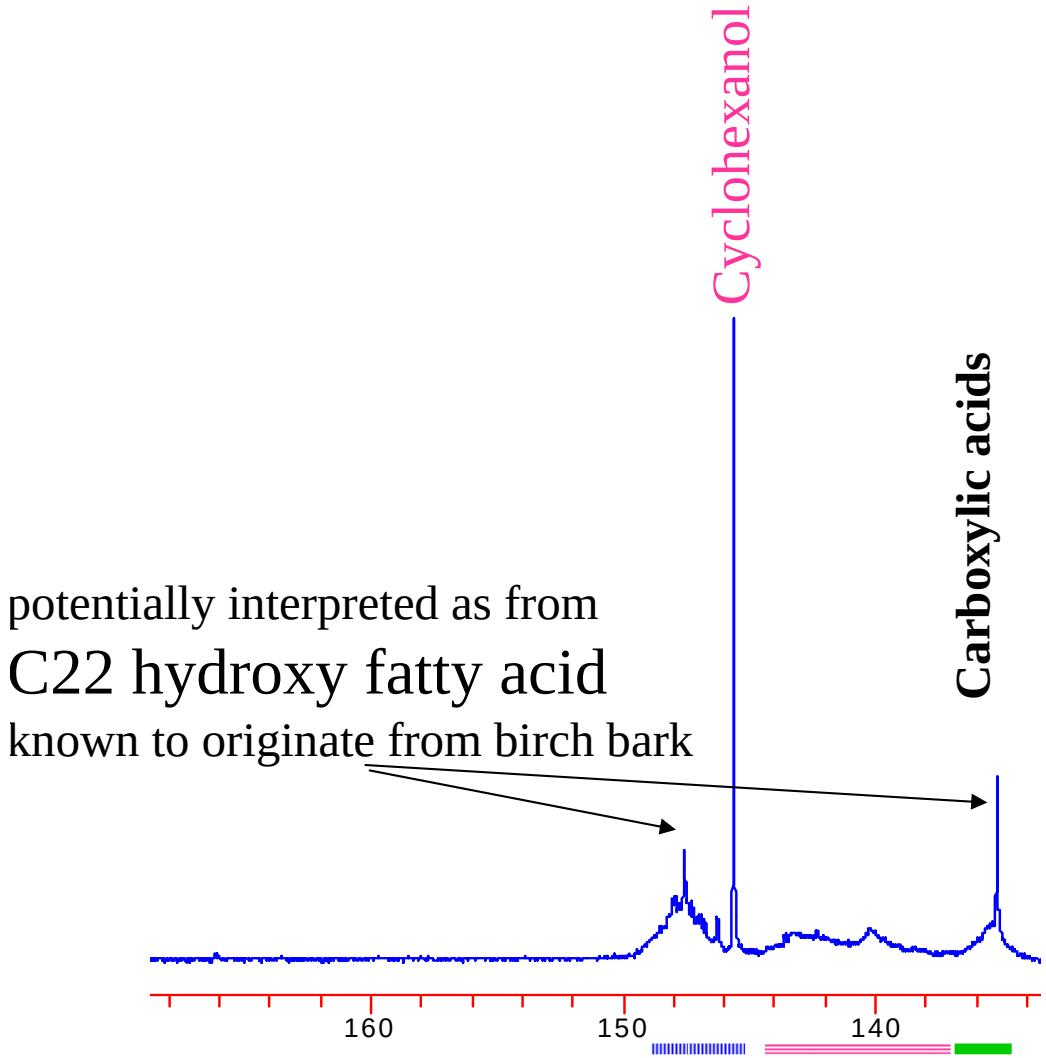


The pulp was <u>acid washed</u> and then extracted again with same solvent

^{31}P NMR of isolated lignin from unbleached SW kraft pulp

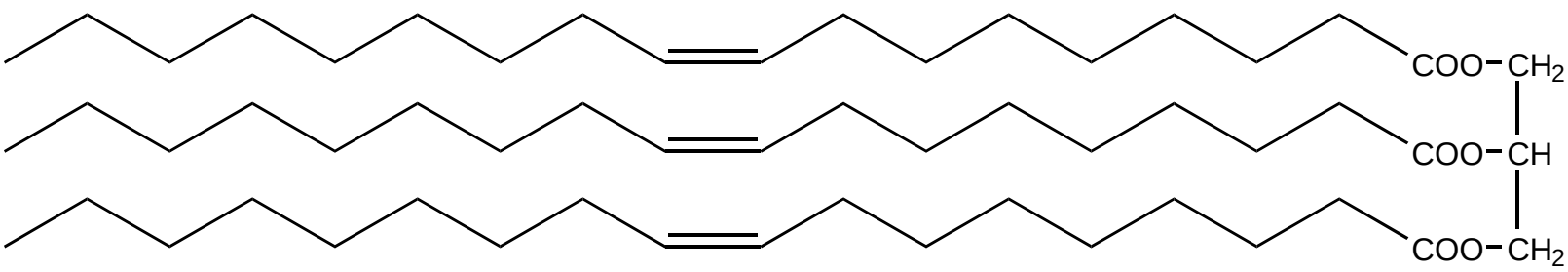


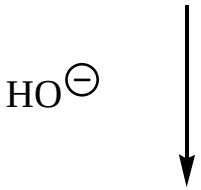
^{31}P NMR of isolated lignin from unbleached HW kraft pulp

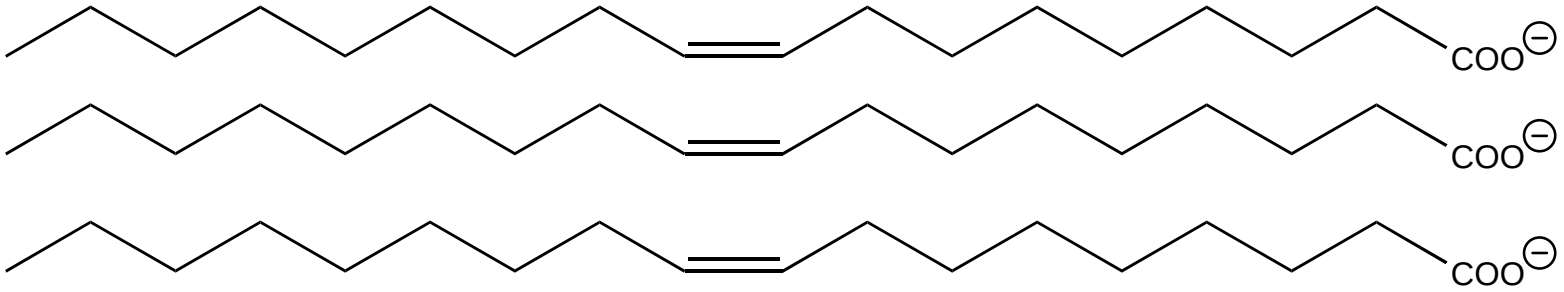


During Alkaline Pulping

Hydrolysis of fat to fatty acid soaps



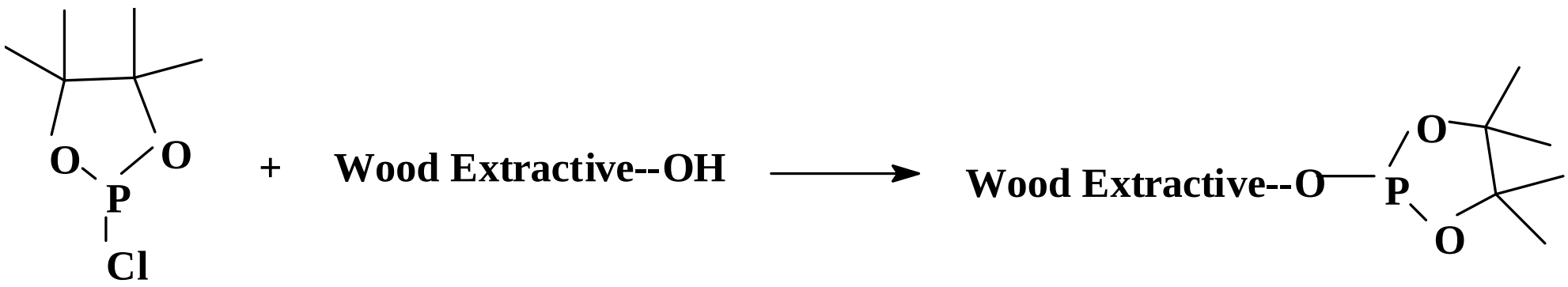




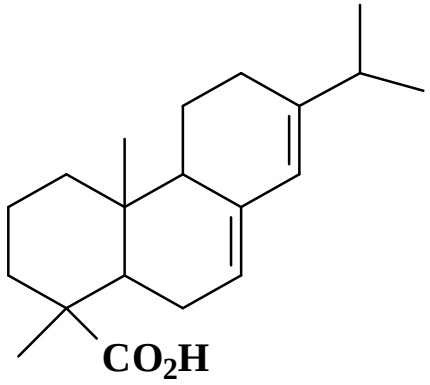
Ca^{2+}

Fe^{2+}

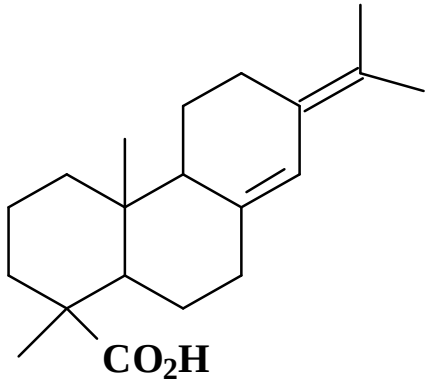
^{31}P NMR Chemical Shift Studies of Wood Resins



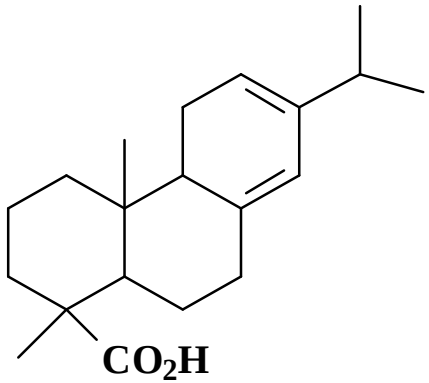
Abietic Acid Derivatives



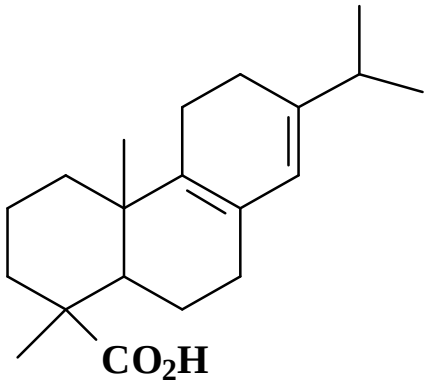
Abietic Acid (135.7 ppm)



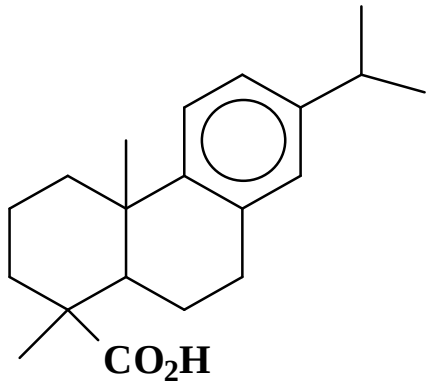
Neobietic Acid (135.0 ppm)



Levopimaric Acid (135.0 ppm)

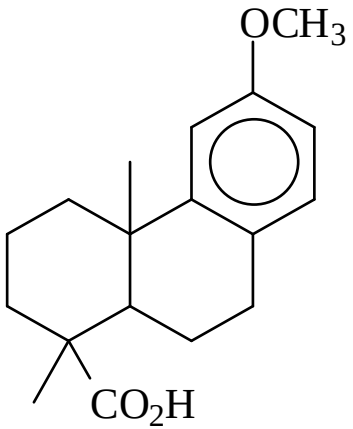


Palustric Acid (135.2 ppm)

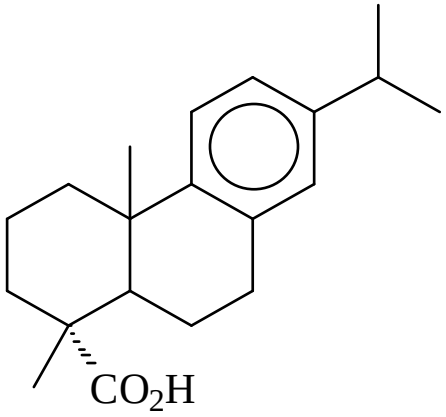


Dehydroabietic Acid (135.1 ppm)

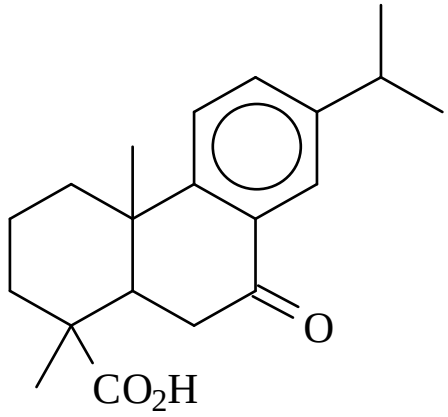
Abietic Acid Derivatives



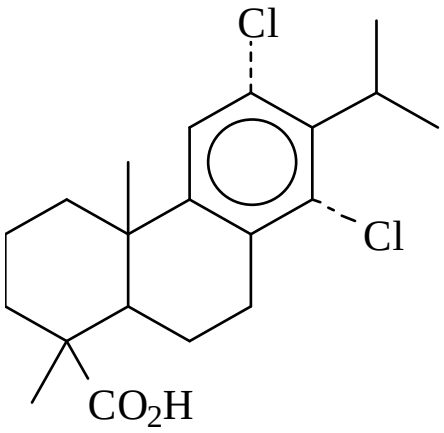
134.7 ppm



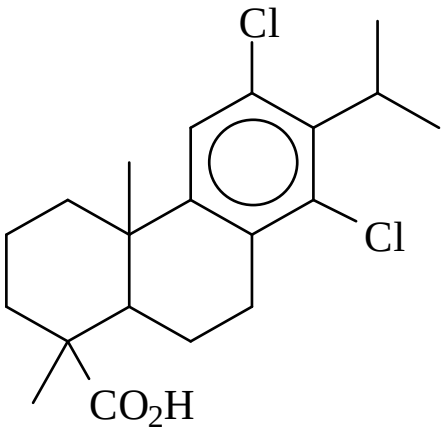
135.1 ppm



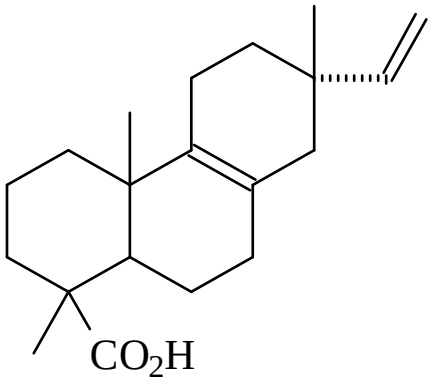
135.7 ppm



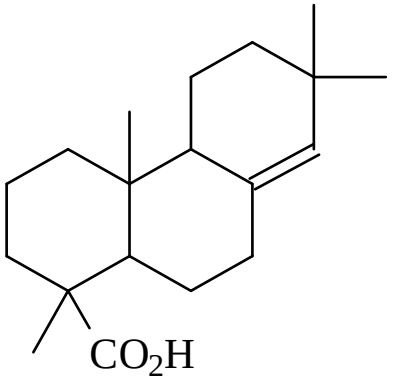
135.2 ppm



135.3 ppm



135.3 ppm



135.0 ppm

Fatty Acids

Saturated Fatty Acid

$CH_3(CH_2)_{16}CO_2H$ 134.7 ppm

$CH_3(CH_2)_{14}CO_2H$ 134.7 ppm

Unsaturated Fatty Acid

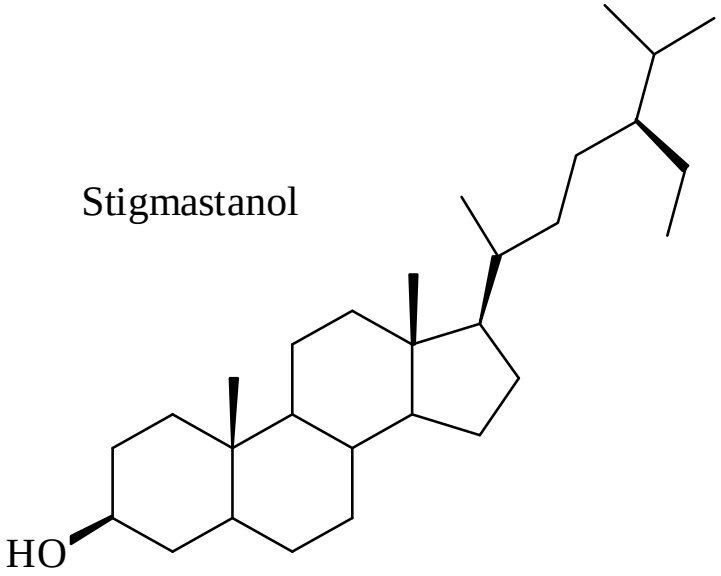
Oleic Acid: $CH_3(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7CO_2H$ 134.7 ppm

Linoleic Acid: $CH_3(CH_2)_4\text{-}CH{=}CH\text{-}(CH_2)_8CO_2H$ 134.6 ppm

Linolenic Acid: $CH_3(CH_2)\text{-}CH{=}CH\text{-}(CH_2)_8CO_2H$ 134.6 ppm

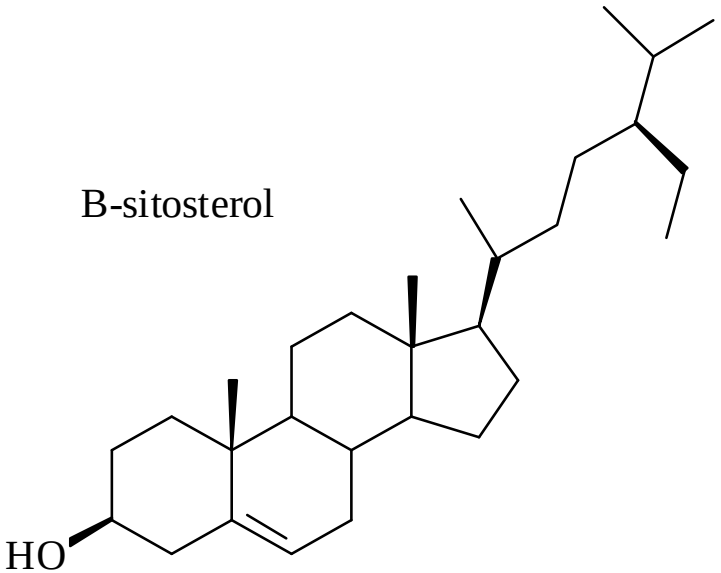
Sterol Derivatives

Stigmastanol



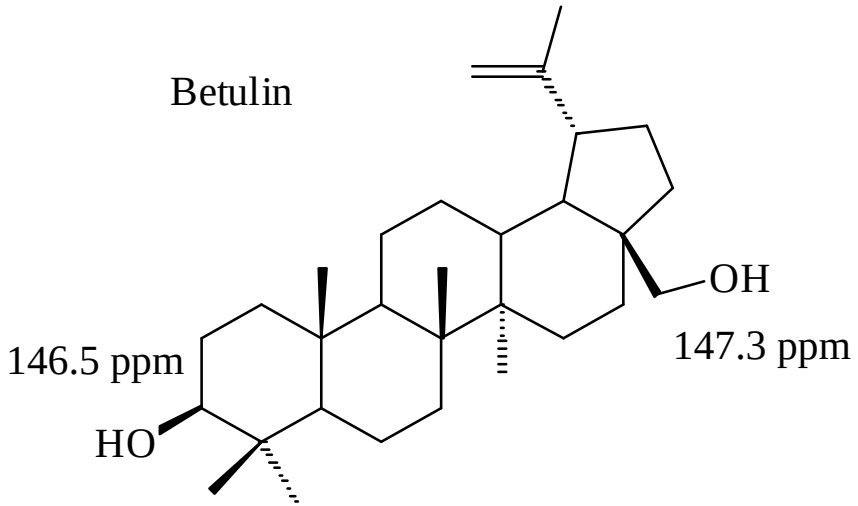
144.8 ppm

B-sitosterol



144.8 ppm

Betulin



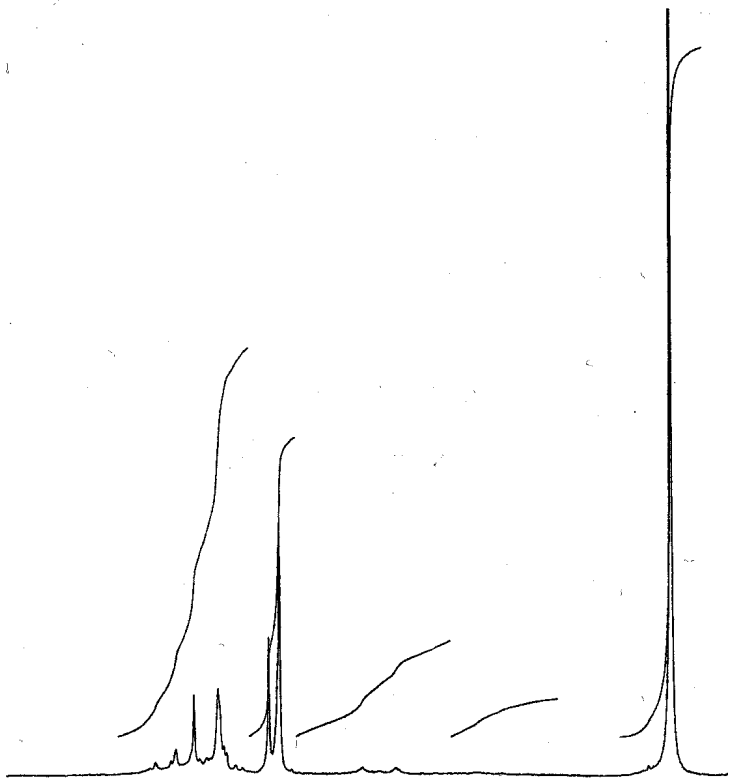
146.5 ppm

147.3 ppm

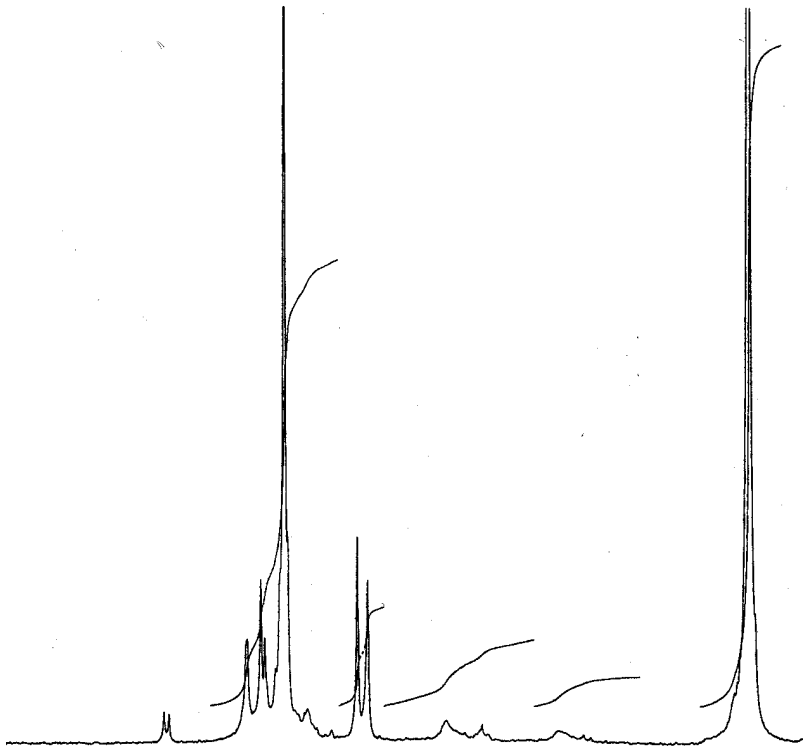
Fatty Alcohols: 147.0 ppm

HW CH_2Cl_2 Extraction

First Extraction

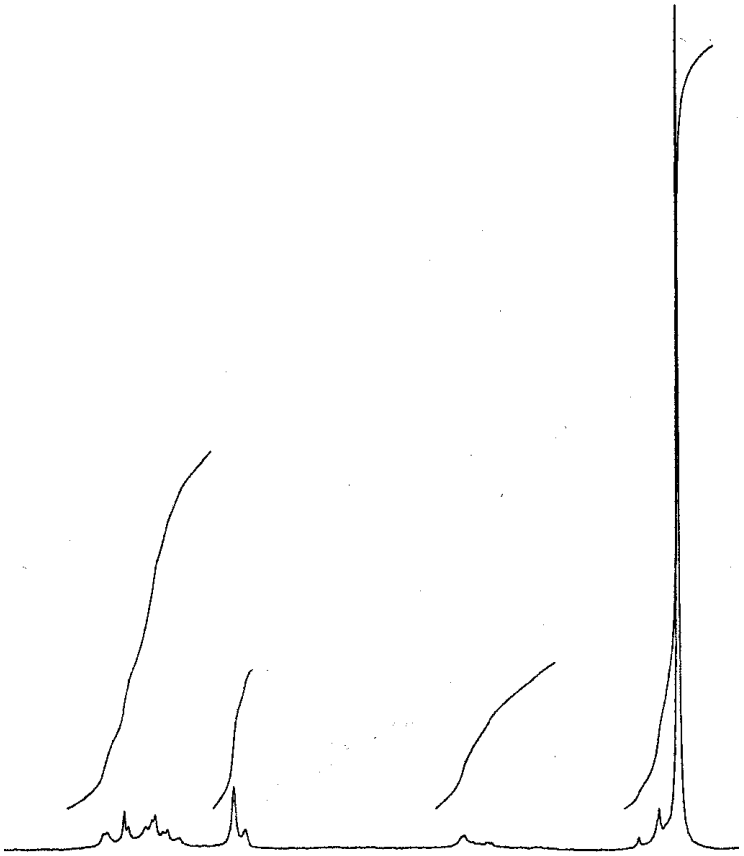


Second Extraction After Acidification

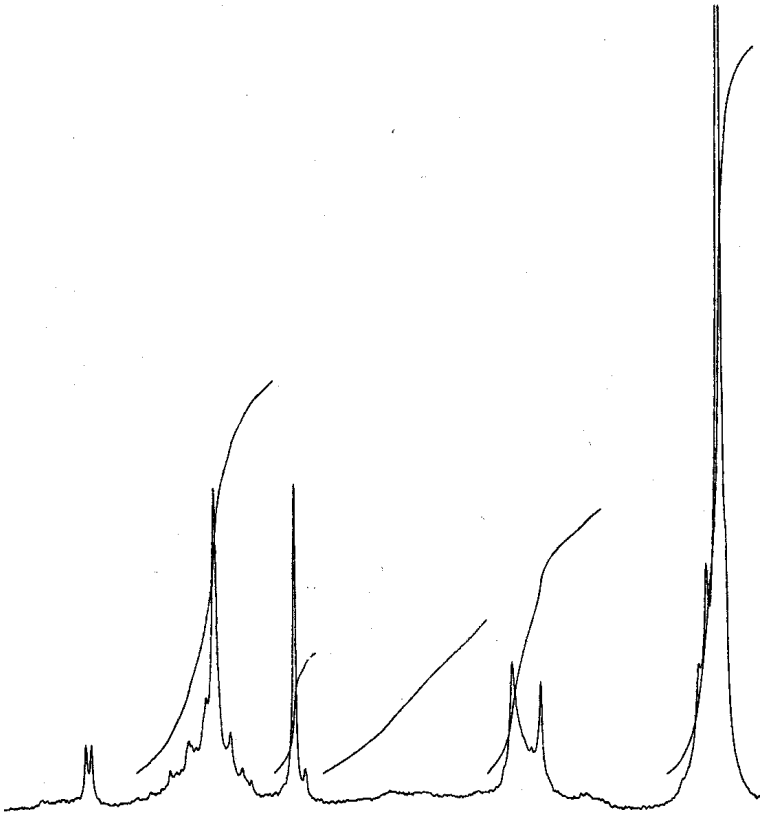


SW CH_2Cl_2 Extraction

First Extraction



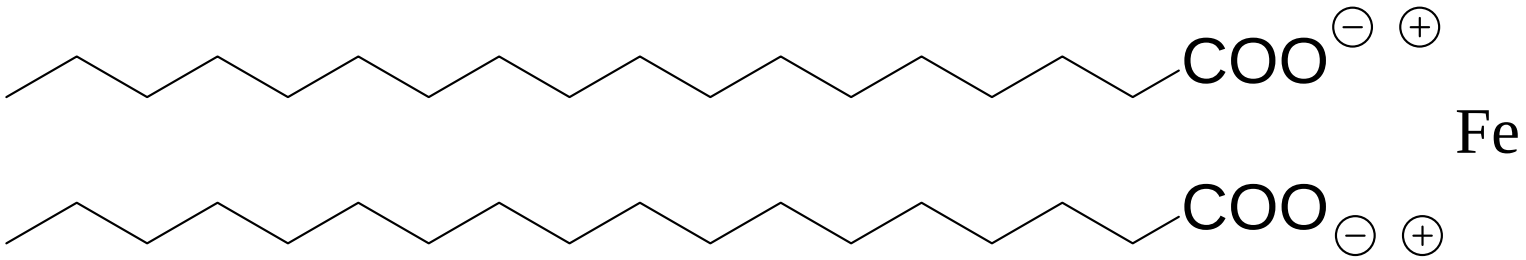
Second Extraction After Acidification



Important Closing Remarks

- Traces of extractives may be most detrimental
  if they simply are <u>assumed to be absent</u>

- Fatty acid soaps with iron forms stronger complexes than with DTPA



This may be the form in which iron is present in pulps

- Long-chained saturated fatty acid salts are difficult to completely protonate

H_2O H_2O

$H_3O^{\oplus}$

H_2O

Conclusions

- Lignin-Extractives-Complexes, LEC, may exists
- Acidification before extraction is a necessity
  for reliable results from pulps that have been alkali treated
- All wood extractives could not be removed by extraction
- Saturated fatty acids in small amounts may disturb analysis
  of isolated lignins by NMR
- A sample purity control is needed
  for reliable ^{1}H, ^{13}C, ^{31}P NMR determinations
- A better standard procedure for extractions is needed