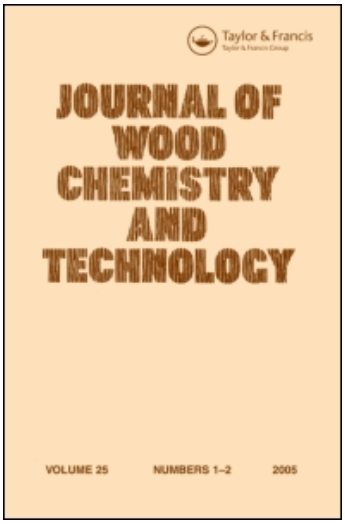

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Thioacidolysis of Lignin: Comparison with Acidolysis

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THIOACIDOLYSIS OF LIGNIN: COMPARISON WITH ACIDOLYSIS

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ABSTRACT

Arylglycerol-ether bonds of lignin samples or model compounds were selectively cleaved by treatment with dioxane-ethanethiol (9/1, v/v) and 0.2 N HBF_4 etherate or 0.2 N BF_3 etherate at 100°C for four hours. Monomers resulting from "thioacidolysis" were identified by gas chromatography-mass spectrometry of their trimethylsily derivatives. Compared to acidolysis (dioxane-water, 0.2 N HCL, 100°C 4h), thioacidolysis yields less complex mixtures of monomers. The monomer yields for lignin thioacidolysis were also higher than for acidolysis. This increase was particularly evident for hardwood lignins.

INTRODUCTION

Alkyl-aryl ether linkages are the main intermonomeric bonds in lignins. Therefore, their cleavage has been extensively studied. Some of the degradation procedures which lead to low-molecular weight products are ethanolysis,[1] acidolysis,[2] and thioacetolysis.[3] Acidolysis was comprehensively studied by Lundquist.[4] It was shown to be a rapid and reliable method of analysis for various samples.[5,6] However, in acidic medium, particularly at high temperature, severe condensation reactions which

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occur in lignin decrease the yield of the monomers recovered from aryl-glycerol ether splitting.[4] These side reactions occur primarily because of the intermediate benzylic cations formed in the acidic media. In the thioacetolysis procedure developed by Nimz, these ions are efficiently converted into a S-benzyl thioacetate derivatives.[3]

The objective of this study was to evaluate the effectiveness of acidolyses using enthanethiol-dioxane and 0.2 N HBF_4 etherate or 0.2 N BF_3 etherate as the acidic reagent. Compared to classical acidolysis using water-dioxane with 0.2 N HCl it was thought that the nucleophilic ethanethiol could potentially displace protonated α-hydroxyl or α-alkoxyl groups and thereby minimize condensation reactions due to the benzylium carbocation; i.e. an S_N2 type reaction,[7] rather than a S_N1 one described for acidolysis mechanisms could occur. Either Lewis or Brønsted acids can be used for cleavage of ethers with thiols.[8] Thus, we tried a typical example of each type, i.e. BF_3 etherate and HBF_4 etherate.

In this study, the thioacidolysis conditions were not optimized. The temperature, reaction time, and acid concentration employed were the same as in acidolysis. Thioacidolyses were performed with softwood and hardwood soluble lignins, and also with an insoluble grass parietal residue. In addition, to aid in interpreting the reactions, guaiacyl and syringyl arylglycerol-β ether dimers were subjected to thioacidolysis.

For comparison purposes, the results of acidolysis of the same lignin samples, as well as several β-O-4 dimers, are shown in Tables 1 and 2.

A typical gas chromatogram of trimethylsilyated (TMS) monomers obtained from acidolysis of the syringyl dimer 5 is shown in Figure 1. The peaks of the syringyl ketones (S) used for quantitative analysis and also some peaks (X) tentatively assigned to TMS syringlypropane monochloride derivatives (see discussion) are indicated in the chromatogram. The complexity of this chromatogram makes it difficult to use quantitatively. Chromatograms obtained from hardwood samples were even more complex.

TABLE 1

Yields[a] of Acidolysis Ketones (%) for Lignin Preparations

Origin	Lignin Fractions	Respective Yields for[b] H	G	S	Total Yield	Monomeric Ratio[b] H/G	S/G
Pine Compression Wood	LR[c]	0.96	7.25	-	8.21	0.13	-
Poplar Wood	LM[c]	-	5.26	3.94	9.20	-	0.75
	LE[c]	-	5.82	7.35	13.17	-	1.26

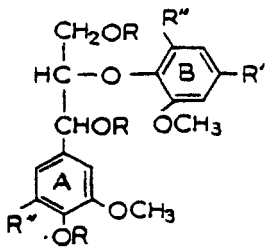
a : not corrected for polyosidic contaminants ; calculations made as in Reference 5 .

b : H : p-hydroxyphenyl , G : Guaiacyl , S : Syringyl Ketones

c : samples prepared according to the procedure previously described .[5] LR from pine and LM and LE from poplar represent respectively 27% , 34% and 16% of the total Klason lignin of the extractive-free wood meal .

TABLE 2

Acidolysis Yields for Dimers



N°	Structure and Isomerism	Reaction yield calculated from : ring A ketones	ring B monomer
1	R,R',R" = H erythro[g]	58	73
	erythro + threo[a]	59	61
2	R' = CH_2OH; R,R" = H erythro + threo[a]	58	60
3	R = $COCH_3$; R',R" = H erythro[a]	69	not determined
4	R" = OCH_3 ; R,R' = H threo[g]	30[b]	63[c]
5	R" = OCH_3 ; R' = CH_2OH ; R = H pure isomer[a]	32	54

a : main ketones from ring A are determined by means of gas-chromatography of their TMS derivatives .[5] Monomers from ring B are analyzed by means of HPLC procedure .[5]

b : impure fraction of 3-oxysinapyl alcohol [9]

c : impure fraction [9]

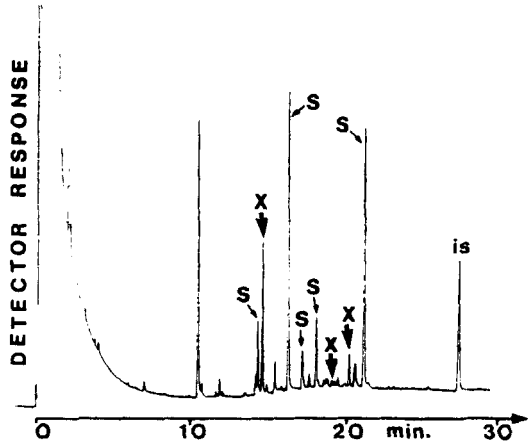


FIGURE 1. GC analysis of TMS acidolysis monomers from dimer 5. S: Syringyl ketones; X: monochloride derivatives; i.s.: internal standard.

EXPERIMENTAL

Material

Dioxane, freshly distilled from a benzophenone-sodium mixture; tetrafluoroboric acid-diethyl ether complex (HBF_4 etherate); boron trifluoride-diethyl ether complex (BF_3 etherate, freshly distilled); and ethanethiol were used throughout the experiments.

Lignin fractions extracted from compression pine wood (Pinus maritima) and poplar (Populus trichocarpa - c.v. Fridzi Pauley), and previously characterized by acidolysis (Table 1); extractive-free parietal residue from wheat straw (Triticum aestivum, c.v. Bastion), with 18.6% Klason lignin; and model compounds 3 and 5, available as pure crystalline products, were degraded by the thioacidolysis method.

Thioacidolysis

Thioacidolyses were performed in duplicate or triplicate as described for acidolysis,[5] but using ethanethiol and HBF_4 or BF_3 etherate instead of water and HCl. Lignin (20 mg), model com-

pound (10 mg), or parietal residue (100 mg) were put in a tube with a Teflon-lined screw cap together with 10 ml of dioxane-ethanethiol (9/1, v/v), 0.2 N HBF_4 etherate or BF_3 etherate, under argon. The tube was then held at 100°C in a oil bath for 4 hours, with occasional shaking. The cooled mixture, adjusted to pH 3-4 with aqueous 0.4 M $NaHCO_3$, was extracted with dichloromethane. The organic extracts, to which was added 1 mg tetracosane in dichloro-methane solution, were dried over Na_2SO_4, and concentrated by film evaporation. The residue was dissolved in dichloromethane (1 ml).

Gas Chromatography (GC), Gas Chromatography-Mass Spectrometry (GC-MS), and High Performance Liquid Chromatography (HPLC) Analyses.

Silylations: an aliquot of the sample solution was dried over Na_2SO_4 and 5 µl was reacted with 50 µl of BSTFA in a 200 µl reaction vial for 24 hours at room-temperature.

GC analyses were carried out on a Girdel model 30 instrument fitted with a 50 m x 0.25 mm i.d. CP SIL 5 fused-silica capillary column (1 µm film thickness - Chrompack), with a Girdel moving needle type injector and a flame ionization detector. The carrier gas was helium (inlet pressure: 1.5 bar) and the temperature was programmed from 180 to 280°C, at 5°C/min.

GC-MS analyses were performed with the same chromatographic system combined with a Nermag R 10-10 B quadrupole spectrometer operating in the electron impact mode (ionization energy: 70 ev).

For HPLC analyses (performed for thioacidolysates of compound 3), sample aliquots were dried under nitrogen, dissolved in a methanolic solution of the internal standard (3,4,5-trimethoxy-cinnamic acid-0.5 mg/ml) and filtered (Millex-SR, 0.5 µm filter unit-Millipore). The experimental conditions for reversed-phase HPLC analyses were the same as reviously described.[5]

Quantitative Analyses

As authentic reference compounds were not available, the thioacidolysis monomers were quantitatively analyzed according to two methods:

Method I: In the thioacidolysis of compound 3, the yield of guaiacol was speculated to be very close to the yield of guaiacyl C_6-C_3 monomers, similar to the acidolysis results for guaiacyl model compounds (Table 2). Therefore, the guaiacol recovery was calculated from HPLC analyses and the amount of guaiacyl phenylpropane monomers, as well as their response factors relative to tetracosane for quantitative gas chromatographic analysis, was estimated from this calculation.

Method II: the GC response factor of an easily prepared monothioethyl guaiacylpropane compound relative to tetracosane was obtained. This compound, the trans-3-(4-hydroxy-3-methoxyphenyl)-1-thioethyl-2-propene (G-CH=CH-$CH_2SC_2H_5$) derivative, was synthesized from eugenol acetate by the method described by Lindeberg[10] for the synthesis of coniferyl alcohol derivatives. The thioethyl derivative was recovered as a pure oil as indicated by ^1H and ^{13}C NMR analyses and GC-MS analysis of the TMS derivative after trimethylsilylation controls.

The GC response factors obtained from methods I and II were used to determine the p-hydroxyphenyl, guaiacyl, and syringyl monomers. This is justifiable on the basis that the TMS derivatives of p-hydroxyphenyl, guaiacyl, and syringyl ketones obtained from acidolyses had very similar response factors.

RESULTS AND DISCUSSION

Qualitative Analysis of the Thioacidolysis Monomers

The GC chromatograms of the TMS derivatives of monomers obtained from samples subjected to thioacidolysis using HBF_4 etherate and BF_3 etherate are shown in Figures 2 and 3, respectively. They are considerably less complex than chromatograms obtained previously for acidolysates[5], e.g. Fig. 1. The monomers derived from thioacidolysis are essentially located in pairs of prominent peaks 6 H, 6 G and 6 S, for the p-hydroxyphenyl, guaiacyl and syringyl derivatives, respectively. With HBF_4 etherate, there are also shoulders 7 G and 7 S.

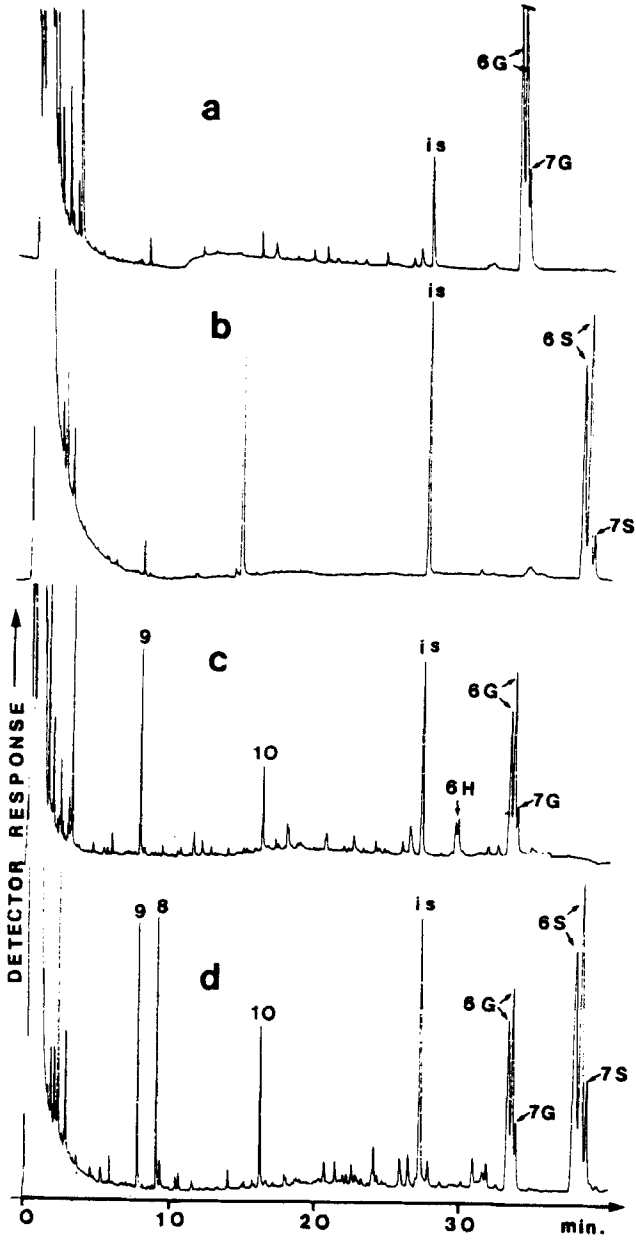


FIGURE 2. GC analysis of TMS monomers from HBF_4 thioacidolysis of a) dimer 3, b) dimer 5, c) pine LR, and d) poplar LE. For peak assignments, see Table 3 and the discussion; i.s.: internal standard. In 2a and 2b, the peaks, with 4 and 16 min. retention times, are derived from ring B (Table 2).

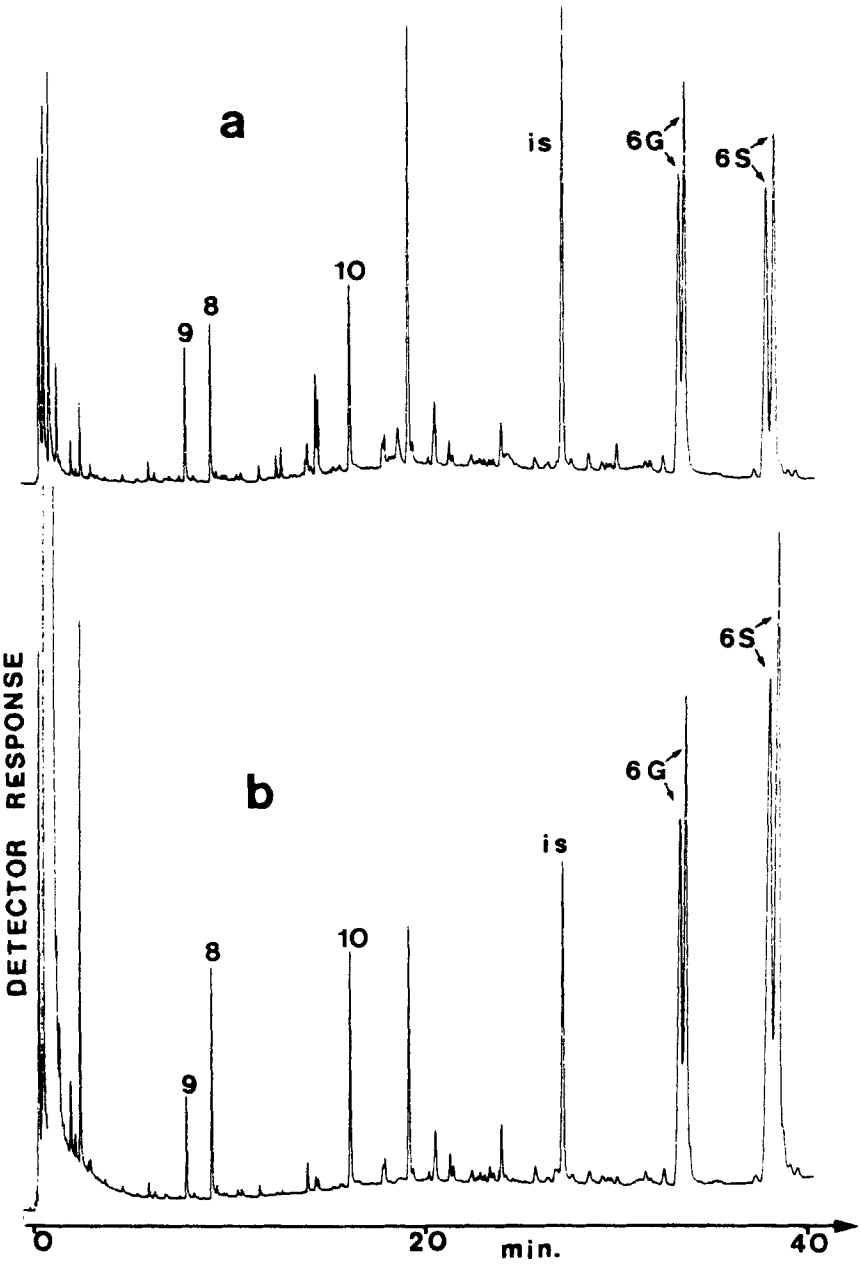


FIGURE 3. GC analysis of TMS monomers issued from BF_3 thioacidolysis of a) poplar LM and b) poplar LE. For peak assignments, see Table 3 and discussion; i.s.: internal standard.

For lignin samples, the area of peaks 6 and 7 corresponded to 85-90% of the total area (calculated for peaks clearly derived from lignin, as determined by GC-MS analyses) and this value increased to 95-97% for mdels 3 and 5. Therefore, thioacidolysis yields were calculated from peaks 6 and 7, since other components were of minor importance. Mass spectrometric data for compounds 6 and 7 are shown in Table 3, with structures tentatively assigned from the fragmentation patterns. Since the pairs of compound designated peak 6 have very similar mass spectra, only the first one of the par is reported in Table 3. The constitutents of peak 6 would be thiethyl phenylpropane isomers, with two chiral carbon atoms. Potential reaction pathways to form compounds 6 and 7 are shown in Figure 4. Along pathway I, the only one with BF_3 etherate and the major one with HBF_4 etherate, the alkoxyl or hydroxyl groups of the side chain are successively converted to oxonium cations and then replaced by the nucleophilic sulfur reagent. It is not clear whether pathway I proceeds by an S_N1 or an S_N2 mechanism, i.e. with or without intermediate carbonium ions. Along pathway II, the minor one with HBF_4 etherate, intermediate enol ethers and carbonium ions are probably formed, similar to acidolysis.

Besides the major monomers, only three other products were of any significance. Product 8, in the poplar samples, corresponds to p-hydroxybenzoic acid, probably linked originally to lignin by means of ester and ether linkages. Vanillic and syringic acids were also found in trace amounts in poplar samples. Products 9 and 10 oserved in lignin chromatograms were tentatively identified as aliphatic thioethyl derivatives from GC-MS analyses. Product 9 (M^+ = 210 and prominent ion 135) could possibly have the structure $CHR_2 - CH_2R$ ($R = SC_2H_5$) and product 10 (M^+ = 284 and prominent ion 135) the structure $CHR_2 - CHR - CH_2R$. They could originate from lignin contaminants, side reactions, or lignin precursors cleaved by thioacidolysis. For example, peak 10 could reflect the occurrence of glyceraldehyde-2-aryl ether structures in lignin, as described with acidolysis results.[11]

TABLE 3

Mass Spectral Data for the Thioacidolysis Monomers in Figures 2, 3 and 5

Peaks	Mass list m/z (%) and Assignments
$\underline{6}$ H	388 (1) = M^+ = H - CHR - CHR - CH_2R 327 (0.6) $\underline{239}$ (100) = H - $^+$CHR 75 (35) , 73 (37)
$\underline{6}$ G	418 (1) = M^+ = G - CHR - CHR - CH_2R 403 (1) $\underline{269}$ (100) = G - $^+$ CHR 75 (23) , 73 (28)
$\underline{6}$ S	449 (3) = M^+ = S - CHR - CHR - CH_2R 433 (2) $\underline{299}$ (100) = S - $^+$ CHR 75 (25) , 73 (33)
$\underline{7}$ G	418 (1) = M^+ = G - CH_2 - CHR - CHR_2 403 (1) 283 (27) = G - CH_2 - $^+$ CHR 222 (35) = G - CH_2 - $^+$ CH 192 (10) $\underline{135}$ (100) = $^+$ CHR_2 75 (35) , 73 (32)
$\underline{7}$ S	448 (4) = M^+ = S - CH_2 - CHR - CHR_2 433 (3) 313 (41) = S - CH_2 - $^+$ CHR 252 (37) = S - CH_2 - $^+$ CH 222 (12) $\underline{135}$ (100) = $^+$ CHR_2 75 (70) , 73 (63)

H : p-Hydroxyphenyl , G : Guaiacyl and S : Syringyl TME rings

R = SC_2H_5

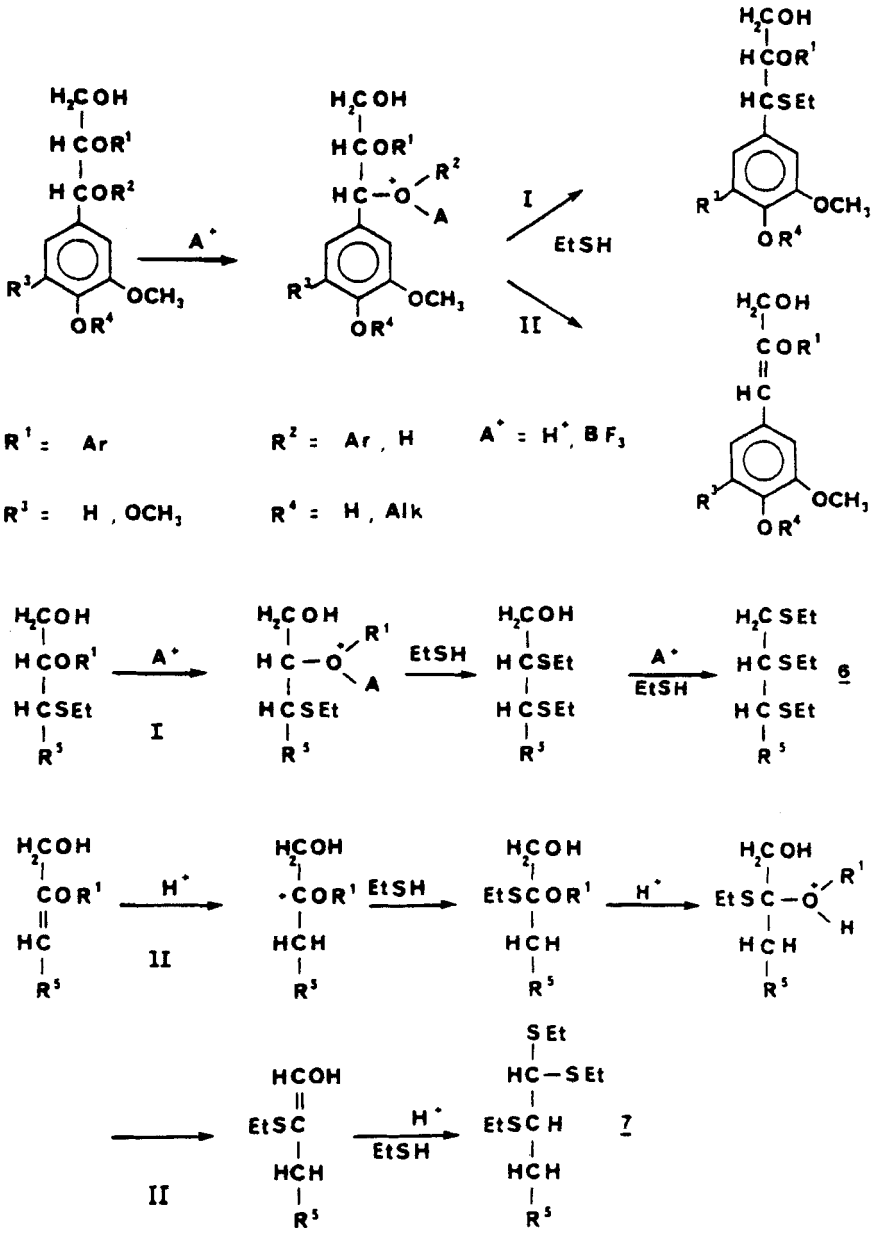


FIGURE 4. Potential reaction pathways I and II affording the main thioacidolysisdolysis monomers 6 and 7 (R^5: syringyl or guaiacyl ring).

Quantitative Analyses of the Primary Thioacidolysis Monomers

Reproducibility of thioacidolyses was ± 5%, simlar to acidolyses. However, silylation of this acidolysis monomers appeared to be easier than acidolysis monomers. Stability of the thioacidolysis monomers was quite good since quantitative results were unchanged after some samples were stored for one year at 4°C. The error introduced by the indirect calibration methods apparently was not very large, since results from the two methods agreed within about 10%.

a. Model Compounds 3 and 5

Monomer yields obtained for compound 3 subjected to acidolysis and to thioacidolysis with HBF_4 etherate were very similar (see Table 4). In contrast, syringyl dimer 5 gave a higher yield of monomers in thioacidolysis than in acidolysis on (Table 4). Since the frequency of condensation reactions is low for model compounds,[4] this improvement cannot be attributed to syringyl intermediates being less prone to condensation side reactions. The improved monomer yield is more likely due to the absence of chlorination reactions which decrease the amount of syringyl ketones recovered in acidolysis. The peaks labelled X in Figure 1 were always present in the chromatograms when hardwood lignin or the syringyl dimer 5 were hydrolyzed with 0.2 N HCl in dioxane-water.[12] These compounds, on the basis of GC-MS analysis, are probably derivatives in which chlorine has replaced a hydroxyl group in the side chain. Such monochloride derivatives, reportedly formed when veratryl compounds were refluxed 3 hours in water-dioxane mixture with 5% HCl,[13] could originate from chlorination of syringyl carbocations. However, it should be noted that analogous monochloride guaiacyl compounds were not observed. Whatever their mechanism of formation, such chlorination reactions are, of course, impossible in the thioacidolyses. The yield calculated from the thioethyl syringyl compounds is therefore higher than the yield calculated only from the main syringyl ketones.

TABLE 4

Thioacidolysis and Acidolysis Monomer Yields for Model Compounds

Yield / Model n°	Calculated with method I	Calculated with method II	Acidolysis Yield for main ketones (Table 2)
3	54	70	69
5	52	57	32

TABLE 5

Thioacidolysis Yields (%)[a] for Lignin and Parietal Residue[b]

Origin	Sample[c]	Reagent etherate of	Yields[a] mean value from methods I and II H	G	S	Total[d]	Monomeric Ratio H/G	S/G
Pine (Compression)	Lignin LP	HBF_4	1.80	10.71	-	12.51 (+ 52%)	0.17	-
Poplar	Lignins							
	LE	HBF_4	-	3.50	16.9	25.4 (+ 95%)	-	1.99
	LE	BF_3	-	9.88	19.9	29.78 (+ 126%)	-	2.01
	LM	BF_3	-	8.36	9.37	17.73	-	1.12
Wheat[b]	Parietal Residue	HBF_4	0.76	10.44	16.32	27.52	0.07	1.56

H : p-hydroxyphenyl , G : guaiacyl , S : Syringyl ketones

a : yields are expressed as equivalent to p-hydroxyphenyl , guaiacyl and syringyl acidolysis main ketones , by multiplying the weight yields of thioethyl compounds respectively with the correction factors $\frac{166}{316}$, $\frac{196}{346}$ and $\frac{226}{376}$. Yields are not corrected for polyacidic contaminants

b : yield expressed as weight percentage of Klason lignin (18.6%)

c : for sample abbreviations , see Table 1

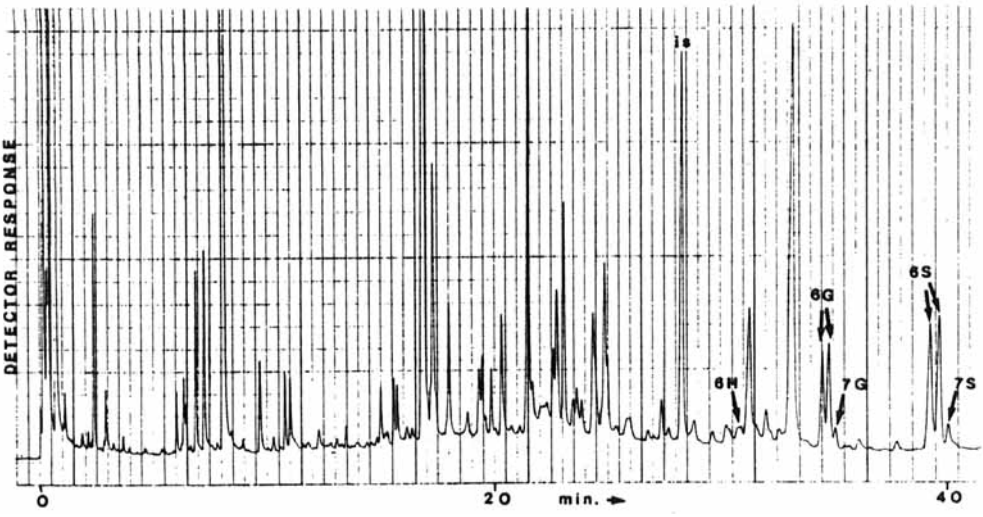


FIGURE 5. GC analysis of the TMS derivatives of thioacidolysis products from wheat parietal residue (HBF_4 etherate). For peak assignments, see Table 3; i.s.: internal standard.

b. Soluble lignins

For comparison purposes the yields in Table 5 are expressed on the same basis as the analogous acidolysis ketones. Since the results from methods I and II were in close agreement, only their mean values are shown. For the lignin samples, yields from thioacidolysis were much greater than for acidolysis for the three monomeric species (Table 5). However, for model compounds the yield improvement isnot as good (5), or is non-existant (3). According to Lundquist,[4] condensation reactions are much more important in lignin acidolysis than in acidolysis of dimeric model compounds. Therefore, when applied to lignin, the thioacidolysis procedure, which should limit these condensation reactions, yields more monomers than acidolysis (+ 50% to + 100%, see Table 5). This increase is more important for syringyl than for guaiacyl structures. In addition, BF_3 etherate seems to afford better yields than HBF_4 etherate. This is probably due to fewer side

reactions and minor reaction pathways, as indicated by the less complex chromatogram. Furthermore, thioacidolysis results (Table 5) confirm the monomeric heterogeneity always observed within poplar lignin fractions.[5]

c. Wheat parietal residue

In contrast to the results for lignins, the chromatogram obtained from thioacidolysis of the parietal residue was highly complex, probably because of the high number of thioacidolysis products from polysaccharides (Figure 5). With classical acidolysis, mainly furfural and hydroxymethylfurfural derivatives are obtained from the parietal polysaccharides.[4] However, despite this complexity, thioacidolysis from parietal residue can be used quantitatively (Table 5), because peaks 6 and 7 are not overlapped by peaks of other components, as confirmed by GC-MS analysis. For wheat (Table 5) and other grass samples, thioacidolysis allows quantitative analysis of all the monomers issued from arylglycerol-ether cleavage. With acidolysis, this was not possible even with high resolution capillary column GC because the TMS derivatives of p-coumaric and ferulic acids, characteristic of grass samples, had the same retention times as the TMS ketonic and enolic derivatives of β-oxy-coniferyl alcohol.[5]

CONCLUSIONS

From this initial study, thioacidolysis performed with BF_3 etherate seems to offer several advantages relative to acidolysis:

(a) The GC chromatograms of the TMS derivatives of the resultant monomers are much simpler, thereby making quantitation easier;

(b) the yield of monomers, particularly the syringyl monomers is much higher, which suggests that the results reflect more closely the monomeric composition of the hydrolyzable structures; and

(c) the procedure gives fairly good reproducibility, with soluble as well as with insoluble samples.

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