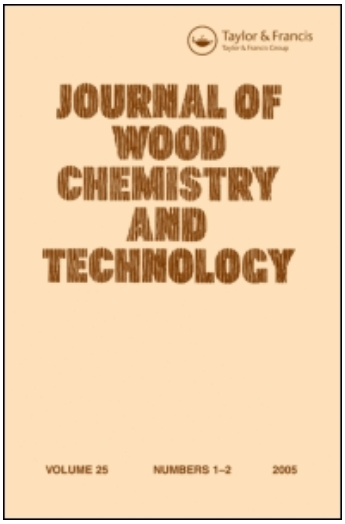

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Formation of C_6 C_2 -Enol Ethers in the Acid-Catalyzed Hydrolysis of Erythro-Veratrylglycerol-β-(2-Methoxyphenyl) Ether

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FORMATION OF C_6C_2-ENOL ETHERS IN THE ACID-CATALYZED HYDROLYSIS OF ERYTHRO-VERATRYLGLYCEROL-β-(2-METHOXYPHENYL) ETHER

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ABSTRACT

Acid-catalyzed hydrolysis of erythro-veratrylglycerol-β-(2-methoxyphenyl) ether in mixed aqueous-organic media yields, in addition to Hibbert's ketones formed via readily hydrolyzable C_6C_3-enol ether intermediates, the cis-and trans-isomers of a C_6C_2-enol ether. The formation of these C_6C_2 isomers involves the elimination of the γ-carbinol group as formaldehyde. Both C_6C_2-enol ether isomers are unexpectedly resistant towards hydrolysis. In aqueous dioxane and ethanol systems, the competing formation of the C_6C_2-enol ethers is increased with increasing concentration of the organic solvent and with increasing reaction temperature.

INTRODUCTION

Under acid-catalyzed hydrolysis conditions, model compounds related to lignins are known to undergo two competing reactions (Figure 1).

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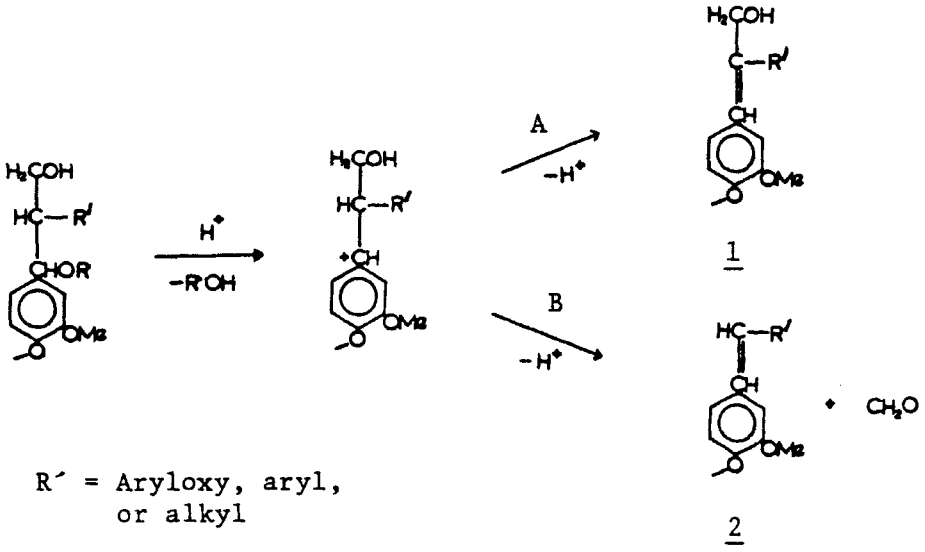


FIGURE 1. Two competing pathways in acid-catalyzed hydrolysis of monomeric units in lignin.

Both pathways yield α,β-unsaturated structures via the elimination of a proton and the α-oxy function. Along pathway A, the proton is released from the β-carbon of the carbonium ion intermediate and the original C_6C_3 skeleton is preserved in an enol ether segment of type 1. In pathway B, on the other hand, the proton is released from the γ-hydroxyl group resulting in the elimination of the γ-carbon as formaldehyde and the formation of the unsaturated structure 2. Competition between pathways A and B has been extensively demonstrated by Lundquist for the hydrolysis of lignin model compounds representing β-5-[1], β-O-4[2] and β-1[1]- lignol structures which all have the 1,3-dioxypropyl side-chain structure 1 in common. The extent of the pathway B can be evaluated from the amounts of formaldehyde released in acid-catalyzed hydrolysis, summarized in Table 1. The results indicate predominance for pathway A in all cases, the importance of the pathway B decreasing in the order:

TABLE 1

Yields of Formaldehyde Obtained in Acid-Catalyzed Hydrolysis of Various Lignin-Related Compounds.

Starting Material		% Formaldehyde on Hydrolysis By Acidolysis	In Boiling 28% H_2SO_4
β-O-4/β-O-H			
Ar'CH(OH)CH(OAr)CH_2OH	(3a)	3[a]	
Ar"CH(OH)CH(OAr)CH_2OH	(3b)	~3[a]	19[b]
Ar"CH(OH)CH(OH)CH_2OH			13[b]
PhCH(OH)CH(OH)CH_2OH			15.5[c]
See also fifth and sixth compounds below			
β-1			
Ar'CH(OH)CH(Ar')CH_2OH		15[a]	
Ar"CH(OH)CH(Ar")CH_2OH		~15[a]	
PhCH(OH)CH(Ph)CH_2OH			71[c]
PhCH(OH)CH(Ph)CH_2OMe			68[c]
PhCH(OH)C(OH)(Ph)CH_2OH			30[c]
$PhCH_2$C(OH)(Ph)CH_2OH			0[c]
β-5			
Dihydro-dehydro-coniferyl alcohol		9[a]	
Aromatic O-Me ether of above		~9[a]	
β-β			
Pinoresinol		0[a]	
Pinoresinol dimethyl ether		0[a]	
Miscellaneous			
Ar'CH_2COCH_2OH	(5a)	0[a]	
Ar"CH_2COCH_2OH	(5b)	0[a]	
Ar'CH=$CHCH_2$OH		0.7[a]	

Ph =  Ar =  Ar' =  Ar" = 

References: a, ref.6; b, ref 7; c, ref.3.

(β-1)- > (β-5)- > (β-O-4)-linked structures. The only 1,3-dioxy side-chain compounds that gave no formaldehyde were the (β-β)-linked pinoresinol and its dimethyl ether; other compounds in Table 1 that gave no, or essentially no, formaldehyde do not have the apparently essential 1,3-dioxy side-chain.

Of the compounds listed in Table 1, veratryl-glycerol-β-(2-methoxyphenyl) ether 3b [1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol], hereafter to be called "diol 3b", and its guaiacyl analogue, diol 3a, incorporate the β-O-4 (arylglycerol-β-aryl ether) structure that represents 47% or more of intermonomeric linkages in lignins[4]. It can be noted that formaldehyde released from diol 3b in boiling 28% sulfuric acid is about five times larger than recovered from "acidolysis" (0.2 N HCl in 9:1 dioxane-water, 4 h at boiling temperature). In the former method, the formaldehyde released is immediately removed by distillation from the reaction zone. Ito, Terashima and Yasuda[5] have demonstrated using diols 3a and 3b that if formaldehyde is left in the reaction zone, it will condense with the starting material to form either 1,3-dioxane derivatives or dioxyl methanes. Such condensation products can represent as much as 30% of the total of all isolated reaction products.

In the acidolysis of diols 3a and 3b pathway A dominates re- resulting in the formation of ketol 5 and its further reaction products ("Hibberts ketones"), as shown in extensive studies by Lundquist[2] (Figure 2). Pathway B appears to represent a minor side reaction only, judging from insignificant yields of formaldehyde and homovanillin 8a. However, it was recently observed in this laboratory[8] in connection with hydrogenolysis studies that pathway B becomes important when the hydrolysis temperature is increased. Formaldehyde release via pathway B in "organosolv pulping"[9] could inhibit dissolution of hydrolyzed lignins. Consequently, further investigation of the hydrolysis of erythro-diol 3b was undertaken in dioxane-water and ethanol-water mixtures, in order to clarify the effect of reaction conditions on the competition between pathways A and B.

EXPERIMENTAL

A. Materials and Methods

Dioxane (Spectroscopy grade) and ethanol (USP 95% grade), without additional purification, were used for the solvents throughout the experiments.

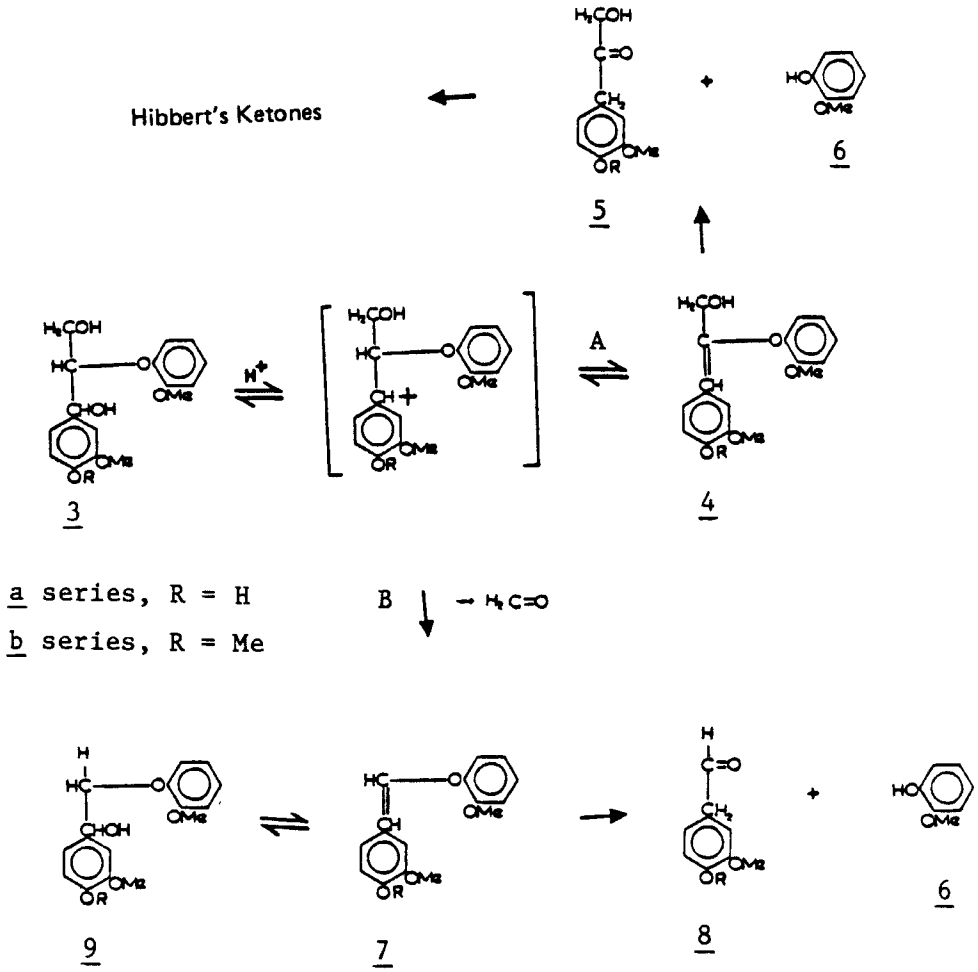


FIGURE 2. Acid-catalyzed cleavage of arylglycerol-β-aryl ether units.

Proton NMR were recorded on Varian T-60 and EM-360 instruments with tetramethylsilane as internal standard and $CDCl_3$ as solvent. IR spectra were taken on a Perkin-Elmer 727B instrument using NaCl solution cells and $CDCl_3$ as solvent. UV spectra were determined on a Perkin-Elmer Model 571 UV-visible spectrophotometer.

GC analyses were run on a Hewlett-Packard Model 5750 instrument using a SE-52 column (6' x 1/8"), flame ionization detector,

N_2 carrier gas (flow rate of 2.2 ml/min), and a temperature program of 130°C for 20 min., then rising to 230°C at 10°C/min.

HPLC analyses were performed on a Waters M 3000 instrument using a reversed phase μ-Bondapak C_{18} analytical column, a UV-detector at 280 nm, and Hewlett-Packard HP-3390A integrator. Two solvent systems [MeCN:MeOH:H_2O (1:7:15) and MeOH:H_2O (2:1)] with a flow rate of 0.4 ml/min were used. The former solvent system was run for 30 min and then changed to the latter for the rest of the run.

GC-MS analyses were obtained using a Hewlett-Packard Model 5985 system. An SE-30 fused silica capillary column (0.242 mm x 30 m), temperature program of 150-220°C (10°C/min), flow rate of 40 ml/min, and ionization energy of 70 ev were used.

B. Synthesis of Model Compounds

erythro-Veratrylglycerol-β-(2-methoxyphenyl) ether (3b), m.p. 96-97.5°C, was prepared by the procedure given in the previous paper[10]. Veratrylglycol-β-(2-methoxyphenyl) ether (9b), m.p. 130-132°C, was kindly synthesized by Mr. Mehdi Meshgini of the College of Forest Resources, University of Washington, using the procedure of Gierer and Noren[11]. Homoveratraldehyde (8b) was prepared by the following modification of the procedure of Ratcliffe and Rodehorst[12]: 0.24 g of 2-(3,4-dimethoxyphenyl) ethanol in 2 ml of CH_2Cl_2 was added to 1.00 g of CrO_3 and 1.6 ml of pyridine in 25 ml of CH_2Cl_2. The reaction temperature was kept at 10 ± 1°C for 25 min and then allowed to rise to room temperature over 10 min. Work up in the specified manner then afforded 0.22 g of undistilled homoveratraldehyde as a pale yellow oil contaminated with only small amounts of veratraldehyde and unreacted 2-(3,4-dimethoxyphenyl) ethanol as shown by IR and GC studies.

C. Analysis of Products of Acid-Catalyzed Hydrolysis of erythro Diol 3b

(1) Hydrolysis Runs

Solutions of substrate (0.015 M) containing hydrochloric acid (0.002 M-0.2 M) were injected in 4-ml quantities into 6-ml glass ampules, which were degassed and then sealed under vacuum. For the reaction temperature 140°C, the ampules were heated in a constant-boiling p-xylene bath. In the case of 170°C runs, the ampules were heated in 30-ml stainless steel autoclaves that also contained 10 ml of solvent as heat-transfer medium. The reactions were terminated in less than one half-life period by cooling the ampules in ice-water. The contents of each ampule were transferred quantitatively to a 10-ml volumetric flask, and water was added to the mark. The resulting solutions were subjected to GC, HPLC and GC-MS analyses. "Acidolyses" were conducted as in the "preparative" procedure of Lundquist and Lundgren[16] under nitrogen.

(2) Analysis by GC and HPLC

When acid-catalyzed hydrolysis products of erythro-diol 3b and glycol ether 9b were analyzed by GC and HPLC, principal peaks were identified by spiking with authentic samples and by GC-MS. The retention times for these compounds are shown in Table 2.

The mass spectrometric data on reaction products are shown in Table 3.

Several attempts were made to isolate the pure cis- and trans-isomers of the C_6C_2-enol ether 7b. These two isomers could be collected as separate HPLC fractions only when using a very small sample. The fractions from such an analytical run, of unknown concentration, had these UV spectral features (in aqueous methanol): first 7b isomer eluted, λ_{max} 270 nm (relative absorbance, RA 1.00), λ_{min} 247 nm (RA 0.47), in-

TABLE 2

Summary of Principal GC and HPLC Peak Retention Times of Acid-Catalyzed Hydrolysis Products

	Retention Times, Minutes						
Technique	Capillary GC-MS		Packed Column GC		Reversed Phase HPLC		
Substrate Hydrolyzed	3b[a]	3b[b]	3b[b]	9b[b]	3b[a]	3b[b]	9b[b]
Products Identified:							
Guaiacol (6)	c	c	2.5	2.5	25	27	27
Aldehyde 8b	3.6	3.6	16	16	32	29	29
Aldehyde 12b	4.6	d	d	--	d	d	--
erythro-Diol 3b	e	e	e	--	43	42	--
Ketone 10b	5.7	--	--	--	d	--	--
Glycol ether 9b	e	e	e,f	e,f	52	51	51
Unidentified					57		
Aldehyde 11b	6.0	--	--	--	d	--	--
Ketol 5b	6.2	6.2	g	--	20	20	--
C_6C_2-Enol ethers 7b	13.4, 14.4	13.4, 14.4	41, 43	41, 43	75, 82	73, 80	73, 80

[a] Hydrolyzed in ethanol-water.

[b] Hydrolyzed in dioxane-water.

[c] Eluted before MS-scanning.

[d] Peak corresponding to this compound not identified.

[e] Not detected.

[f] GC of pure, unhydrolyzed 9b afforded only the two peaks for the enol ethers 7b.

[g] Not identified, but apparently one of three occasionally significant peaks at 17, 25, and 26 min.

TABLE 3

Principal Mass Spectral Peaks of Major Acid-Catalyzed Hydrolysis Products.

Compound	m/e (Relative Abundance)
Aldehyde 8b	180(M^+,22.5),152(12.4),151(100),135(9.0), 108(5.6),107(16.9),106(10.1),105(11.2), 91(10.1),77(13.5)
Ketol 5b	211(2.7),210(M^+,22.5),152(9.7),151(100), 135(3.7),108(3.1),107(9.5),106(4.9),105 (4.4),91(3.3),77(4.8)
Enol ether 7b (more volatile isomer)	288(5),287(20),286(M^+,100),271(20),257(25), 242(7),226(31),211(7),185(5),169(5),165(5), 151(18),149(7),135(8),133(8),121(9),119(7), 118(7),109(5),107(7),105(7),95(9),92(15), 91(14),89(9),77(37)
Enol ether 7b (less volatile isomer)	288(5),287(21),286(M^+,100),271(23),257(24), 242(7),226(34),211(8),193(33),185(5),169(5) 165(14),164(11),151(100),149(11),135(12), 133(11),124(5),121(13),119(11),118(6),109(7), 107(15),105(13),95(15),92(19),91(20),89(12), 77(53)
Aldehyde 12b	192(M^+,100),163(83),133(42),91(34),77(49)
Ketone 10b	196(15.7),195(100),167(24.7),151(5.6),139 (60.7),124(16.9),108(9.0),95(6.7),77(14.6)
Aldehyde 11b	209(13.6),165(13.6),151(27.3),107(13.6), 106(11.4),103(100),91(11.4),78(11.4),77 (15.9)

flections at 275 nm (RA 0.99) and 293 nm (RA 0.48), RA_{280} 0.92; second 7b isomer eluted, λ_{max} 268 nm (RA 1.00), λ_{min} 245 nm (RA 0.45), inflections at 275 nm (RA 0.90) and 300 nm (RA 0.48), RA_{280} 0.83. (RA's are independent for each isomer). Literature UV data[13] for the analogous C_6C_3-enol ether 4a: λ_{max}^{EtOH} = 269 nm

(ε = 21,184) and 297 nm (ε = 8,129), λ_{min}^{EtOH} = 242 nm (ε = 8,129) and an inflexion at 278 nm (ε = 17,000 in ethanol).

In a small-scale preparative HPLC run, a 20-mg sample of enol ethers 7b (prepared by 0.002 M HCl-catalyzed hydrolysis of 9b in 1:1 dioxane-water at 170°C for 1.5 h) was obtained as a waxy mixture of geometric isomers, since complete resolution was not possible at these column loadings. Rechromatography (HPLC) of this isomer mixture showed it to be free of material other than 7b. In 95% ethanol, it had λ_{max} 268 nm (ε 15,800) with inflections at 274 nm (ε 15,100) and 297 nm (ε 8,430); at 280 nm, it had ε 14,100. NMR: δ3.93 (s, 9, CH_3O); 5.61 (d, ~0.5) and 6.62 (d, ~0.5) [$J_{\alpha,\beta}$ = 7 Hz; cis C_α and C_β H, respectively] ; 6.34 (d, ~0.5) and 7.06 (d, ~0.5) [$J_{\alpha,\beta}$ = 13 Hz; trans C_α and C_β H, respectively] ; 6.88 and 7.06 (narrow multiplets partially overlapping the 7.06 d, 7, aryl H).

Attempts to increase the HPLC sample size or to use highly concentrated samples not only failed to produce well defined peaks but also generated several extra unknown peaks. This phenomenon occurred not only on HPLC of the hydrolysis products of both compounds 3b and 9b but also on HPLC of crude C_6C_2-enol ether 7b samples kindly prepared from 9b by Mr. M. Meshgini using alternative methods.

D. Quantitative Determination of C_6C_2-Enol Ethers 7b and Guaiacol (6)

HPLC was used for this purpose. The amounts of the C_6C_2-enol ethers 7b (cis- and trans-combined) and guaiacol (6) were calculated from the peak areas of the HPLC chromatograms of the acid-catalyzed hydrolysis products of erythro-diol 3b, using 280-nm molar absorptivity values of 14,100 for the enol ethers and 2,410 (determined using a redistilled commercial sample) for guaiacol.

RESULTS AND DISCUSSION

A. Evidence of C_6C_2-Enol Ether Production

In acid-catalyzed hydrogenolysis studies on erythro-diol 3b[8], it was found that C_6C_2-products, including the guaiacyl ether of veratrylethanol, are produced. It therefore was presumed that the parent intermediate was enol ether 7b [Chemical Abstracts' name 1,2-dimethoxy-4-[2-(2-methoxyphenoxy)ethenyl]-benzene]. Confirmatory evidence includes the following.

Veratrylglycol-β-(2-methoxyphenyl) ether (9b) [Chemical Abstracts' name 3,4-dimethoxy-α[(2-methoxyphenoxy)methyl]benzenemethanol] on acidolysis afforded a reaction mixture rich in the same low polarity pair of products that were obtained from erythro-diol 3b (see HPLC data in Table 2) and assumed to be the geometric isomers of enol ether 7b. These compounds therefore could not have a C_3 side chain.

On gas chromatography on the packed column, glycol ether 9b, with or without preliminary acidolysis, afforded the pair of peaks designated 7b isomers. That a benzylic alcohol like 9b would pyrolytically dehydrate seems reasonable (9b has been reported to fragment in part to enol ether 7b during mass spectrometry[14]).

The mass spectra of this pair of GC peaks are very similar. They both have, as parent and base peaks, ones of m/e 286, appropriate for structure 7b. The two fragment in nearly identical ways; the only two major differences are that the less volatile isomer affords over five times as much m/e 151 fragment as the earlier eluting isomer and uniquely affords a very significant amount of m/e 193 fragment.

As noted, mass spectrometry of the glycol monoether 9b has been reported[14] to give enol ether 7b as one fragmentation product. The less volatile of our pair of isomers contains every peak in the reported spectrum of 9b (peaks at m/e 286, 271, 257, 225, 165, 164, 151, 149, 124, and 109) except ones whose

assigned structures indicate they could only have come directly from 9b. The spectrum of the more volatile isomer matches nearly as well, lacking only the peaks at 164 and 124. It therefore seems likely that the just listed 9b MS peaks are at least partly due to further fragmentation of the 7b peak at m/e 286 and that the similarity between the published and present spectra gives strong support to our structure assignment.

The UV spectra of the pair of low polarity compounds isolated from 3b or 9b hydrolysis products by HPLC closely approximate each other and that published by Sano[13] for the guaiacyl C_6C_3-enol ether 4a (see Experimental).

The NMR spectrum of the mixture of these low polarity products was compared with that of the cis/trans mixture of isomers of the compound identical to enol ether 7b but having an acetoxy group in place of the 4-methoxy group of the C_6C_2-unit. Obst, Landucci, and Sanyer[15] report for this enol ether vinyl proton doublets ($J_{\alpha,\beta}$ = 7 Hz) at 5.53 and 6.57 δ for the cis isomer and a second set of doublets ($J_{\alpha,\beta}$ = 13 Hz) at 6.23 and ~7δ ("second doublet obscured by the aromatic multiplet") for the trans isomer. The data in the Experimental section are in excellent agreement, again confirming the enol ether 7b structure assignment.

B. Hydrolysis of erythro-Veratrylglycerol-β-(2-methoxyphenyl) Ether (3b) in Dioxane-Water Media.

The hydrolysis of 3a has been studied in detail by Lundquist[6,16] under standard acidolysis conditions (0.2 M HCl in dioxane-water, 1:1 by volume, 4 h at 100°C) and altogether ten reaction products have been identified. When the acidolysis of erythro-diol 3b was repeated in this study, HPLC analysis largely confirmed the previous results[16] (Figure 3a). Thus, ketol 5b and guaiacol (6) were clearly the dominant products and no indication of the presence of homoveratralde-

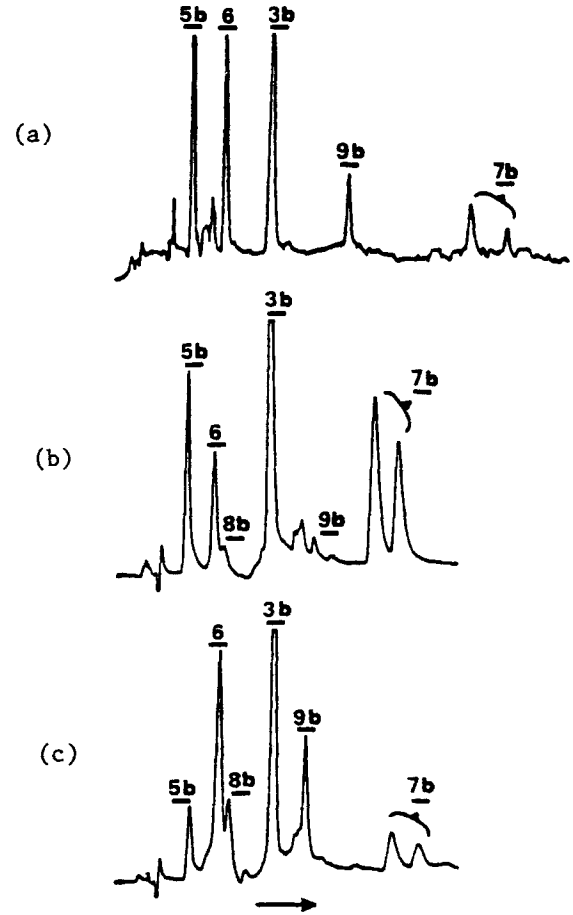


FIGURE 3. HPLC chromatograms for dioxane-water hydrolysis products of erythro-diol 3b: (a) Standard acidolysis (9:1 dioxane-water, 0.2 N HCl, 240 min. at 100°C); (b) 9:1 dioxane-water, 0.002 N HCl, 45 min. at 170°C; and (c) 1:9 dioxane-water, 0.002 N HCl, 45 min. at 170°C. (5b: monomeric ketol, 6: guaiacol, 8b: homoveratraldehyde 3b: starting substrate 9b: C_6C_2-glycol ether, 7b: C_6C_2-enol ethers)

hyde (8b) was found. However, three previously unidentified C_6C_2-products were also present, albeit in relatively small quantities. These were the cis and trans isomers of the C_6C_2-enol ether 7b and the corresponding hydration product, glycol ether 9b. The presence of enol ethers 7b, combined with the absence of their hydrolysis product, homoveratraldehyde (8b), clearly demonstrates the resistance of these ethers towards acid-catalyzed hydrolysis. In contrast, the corresponding C_6C_3-enol ethers 4b are instantaneously hydrolyzed to ketol 5b, and no peak corresponding to enol ethers 4b was discerned in the HPLC chromatogram.

When the hydrolysis in dioxane-water was carried out at higher temperatures and lower acidities, the proportion of enol ethers 7b in the product mixture drastically increased as shown in Figure 3b, illustrating the chromatogram obtained under the conditions of 0.002 M HCl and 170°C. At the same time a small peak indicating the presence of homoveratraldehyde (8b) appeared. This observation suggested that high reaction temperatures favor pathway B; that is, formation of C_6C_2-enol ethers 7b via formaldehyde elimination. In addition, it was observed that at any given reaction temperature, pathway B was also promoted by increasing concentrations of dioxane in the reaction medium (Figure 3c).

An estimate of the ratio of the rate constants for pathways A and B can be based on the fact that essentially all guaiacol found is generated by the former pathway, while pathway B results in near-quantitative conversion to enol ethers 7b. Thus, the following equation is obtained:

$$\frac{k_B}{k_A} = \frac{\text{moles of } C_6C_2\text{-enol ethers 7b formed}}{\text{moles of guaiacol released}}$$

The equation is, of course, not completely precise because some hydrolysis of the C_6C_2-enol ethers does occur and, also, a small part of them are converted to the glycol ether 9b. The error caused by these simplifications, however, is not large.

The rate constant ratio is shown as a function of dioxane concentration in Figure 4, measured at temperatures of both 140 and 170°C. It can be seen that pathway A is the dominant one at all conditions studied. The relative rate for pathway B, that is, of the formation of the C_6C_2-enol ethers, is promoted by increasing concentrations of dioxane in the reaction medium and, to some extent, by increased reaction temperatures.

In an earlier paper[10] the magnitude of k_A for diol 3b was investigated as a function of dioxane concentration. It was found that the rate of guaiacol release becomes significantly faster as the concentration of dioxane is increased in the reaction medium. It follows, then, that increasing dioxane concentrations accelerate the reaction rate along both pathways. The accelerative effect is, however, more pronounced for pathway B.

C. Hydrolysis in Ethanol-Water Media

The formation of the C_6C_2-enol ethers is not limited to dioxane-water systems, but occurs also in mixed ethanol-water media, as shown in Figure 5. In addition, minor products found along pathway B are represented by homoveratraldehyde (8b) and glycol ether 9b. The approximate k_B/k_A ratios increase with increasing concentration of the organic component, in conformity with the observations made in dioxane-water systems. However, since earlier studies[10] have shown that in ethanol-water systems the rate of guaiacol release is essentially independent of the ratio of the two components, the effect of increased ethanol concentrations is limited to the acceleration of pathway B. It should be noted also that the rate constant ratio at 140°C is uniformly lower than in dioxane-water systems while at 170°C it is higher. At high ethanol concentrations, pathway B may become the dominant one.

A cursory GC-MS analysis on the monomeric fraction obtained in the hydrolysis in ethanol-water deomonstrated the presence of the expected components ketol 5b and ethoxy ketone 10b[17] (see Tables 2 and 3). In addition, the ethoxyaldehyde 11b and traces

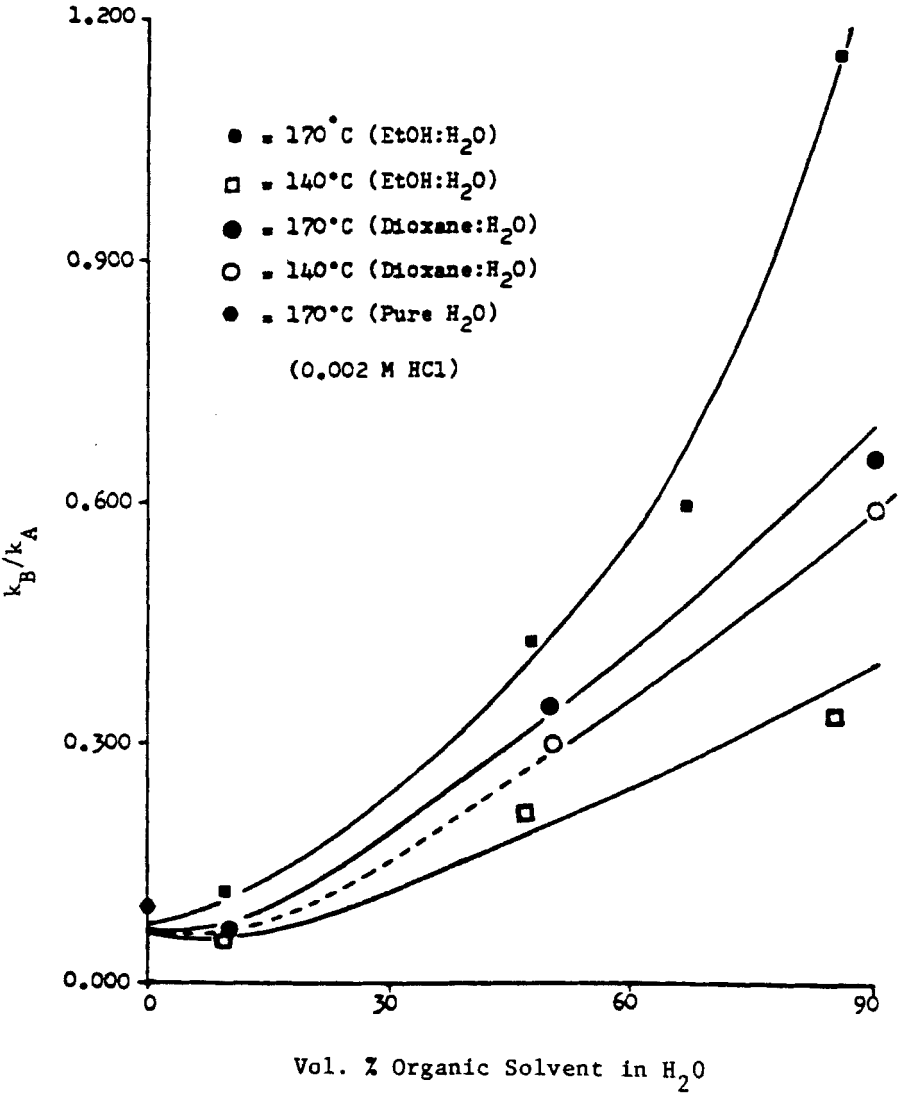


FIGURE 4. Effect of solvent composition and reaction temperature on the ratio of rate constants k_B/k_A in the hydrolysis of erythro-diol 3b in dioxane-water and ethanol-water mixtures.

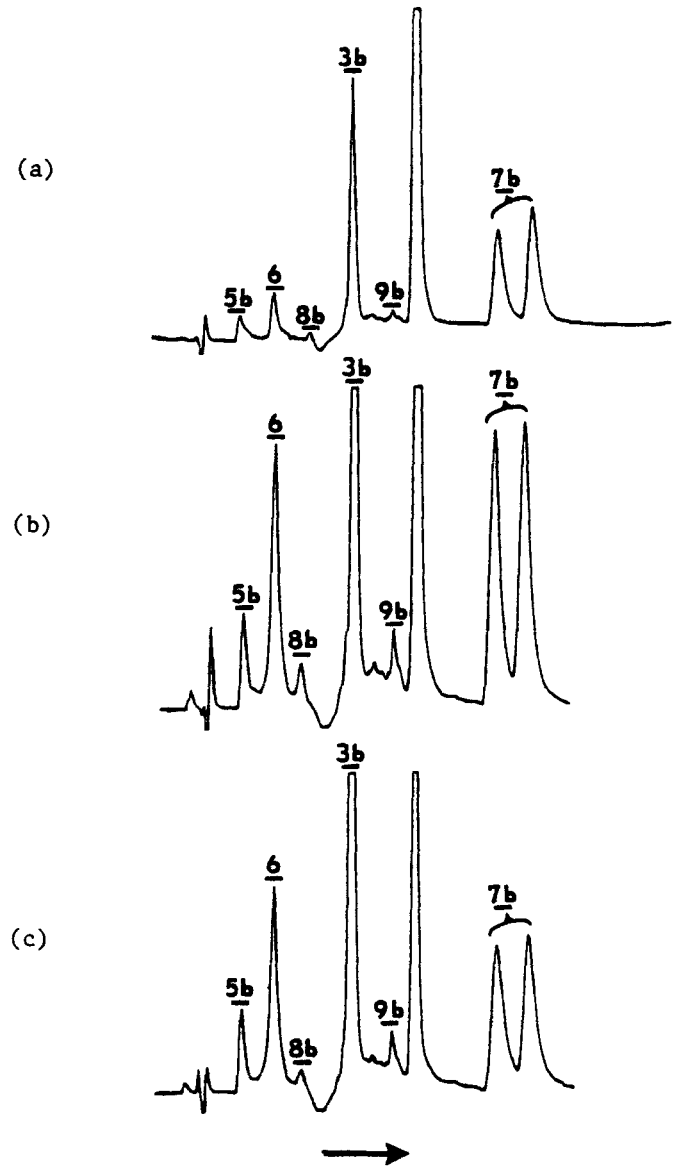
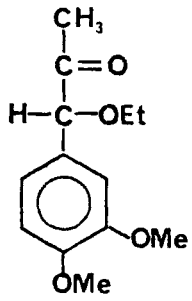
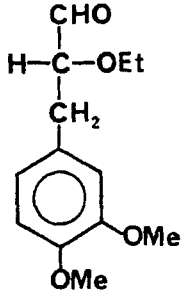


FIGURE 5. HPLC chromatograms for the hydrolysis products of erythro-diol 3b in ethanol-water containing 0.002 M HCl at (a) 9:1 ethanol-water, 300 min. at 170°C; (b) 7:3 ethanol-water, 240 min. at 170°C; and (c) 1:1 ethanol-water, 210 min. at 170°C. (5b: monomeric ketol, 6: guaiacol, 8b: homoveratraldehyde, 3b: starting substrate, 9b: C_6C_2-glycol ether, 7b: C_6C_2-enol ethers)

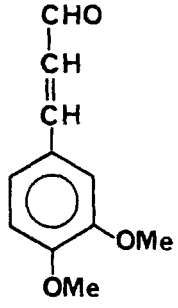
of coniferaldehyde methyl ether 12b were detected in the reaction mixture.



10b



11b

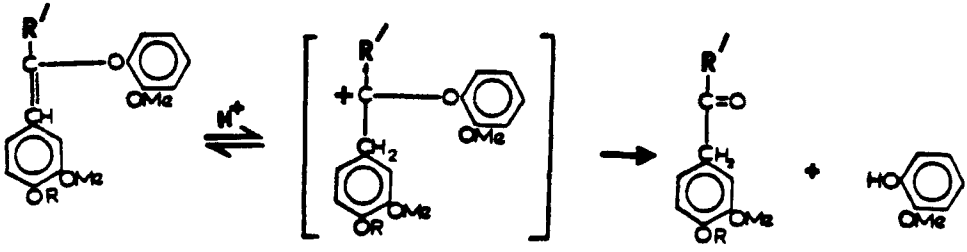


12b

D. Mechanistic Consideration

The results obtained in both dioxane-water and ethanol-water media indicate that increasing the concentrations of these organic solvents favors the deprotonation of the γ-OH over the removal of the β-carbon proton in the benzylic carbocation intermediate. The former proton removal is accelerated by organic solvents such as dioxane and ethanol, while only dioxane promotes proton removal from the β-carbon. The more pronounced temperature effect seen in the ethanol-water system is probably due to a higher activation energy requirement than that for the dioxane-water system during the formation of the C_6C_2-enol ethers 7b. These differences in relative activation energies and relative accessibilities of the β-carbon proton versus γ-OH proton may reflect differing conformation and degrees of solvation of the benzylic carbocation under the differing temperature and solvent conditions.

The facile hydrolyzability of the C_6C_3-enol ether 4b in comparison with the corresponding two-carbon enol ether 7b may be ascribed to the relative stabilities of the respective β-carbocation intermediates 13 and 14 (Figure 6), formed by



6

4: $R' = CH_2OH$ 13: $R' = CH_2OH$ 5: $R' = CH_2OH$

7: $R' = H$ 14: $R' = H$ 8: $R' = H$

FIGURE 6. Mechanism of the acid-catalyzed hydrolysis of C_6C_3- and C_6C_2-enol ethers.

protonation of the enol ethers. The extra substituent on carbocation 13 formed from the C_6C_3-enol ether 4b should make it more stable and, therefore, more readily generated than carbocation 14 derived from the C_6C_2-enol ether 7b.

CONCLUSIONS

The results obtained on the acid-catalyzed hydrolysis of the arylglycerol-β-aryl ether model 3b have important implications concerning solvolytic removal of lignin from lignocellulosic biomass materials, including wood[9]. Approximately one-half of the linkages present in lignin are of the type represented by the model compound 3b and an extensive hydrolytic cleavage of these bonds is probably the most important factor in the acid-catalyzed conversion of the lignin macromolecule to extractable fragments. The results suggest that conditions favoring the conversion of arylglycerol-β-ether units to C_6C_3-enol ethers (pathway A) are optimal for extensive delignification since such ether structures undergo an apparently immediate

hydrolytic cleavage. In contrast, the C_6C_2-enol ether structures formed by pathway B are resistant to acid-catalyzed hydrolysis.

Another potentially interfering factor to delignification consists of the probable release of formaldehyde in the formation of C_6C_2-enol ether structures. Formaldehyde is known to condense readily with lignin resulting in the formation of methylene-cross links between aromatic rings. Since formaldehyde can also be released from structures other than aryl-glycerol-β-ethers, such as β-1 and β-5 lignol structures (Table 1), it is conceivable that formaldehyde release plays a major role in acid-catalyzed condensation processes of lignins.

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