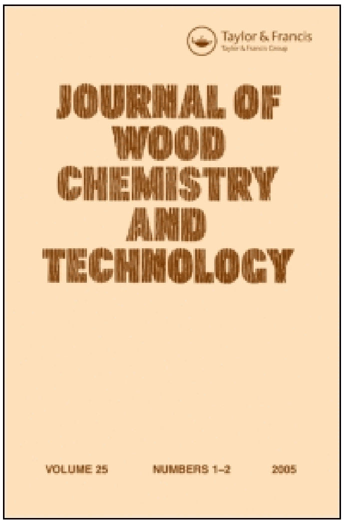

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BEHAVIOR OF LIGNIN IN ORGANIC ACID PULPING. II
REACTION OF PHENYLCOUMARANS AND 1,2-DIARYL-1,3-PROPANEDIOLS WITH ACETIC ACID

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ABSTRACT

In order to explain the behavior of phenylcoumaran and 1,2-diaryl-1,3-propanediol structures in acetic acid pulping, their lignin model dimers in the presence of creosol as a lignin aromatic nucleus model were cooked in 90% acetic acid at 180°C.

About 50% of phenolic phenylcoumaran was consumed during a 3 hour reaction to yield phenylcoumarone, a stilbene derivative and a condensation product, but the non-phenolic model was very stable and was recovered as an acetate. On the other hand, phenolic and non-phenolic 1,2-diaryl-1,3-propanediols were unstable and were degraded within 1 hour to give stilbene derivatives as main products together with diarylmethanes and condensation products.

INTRODUCTION

In the previous communication[1)] of this series, the behavior of phenolic and non-phenolic arylglycerol- β-aryl ether structures during acetic acid pulping was described. It was found that these structures are not only degraded by hydrolysis as a main delignification reaction, but also polymerized by intermolecular condensation reactions. In addition to these reactions, a part of the phenolic unit was suggested in a model experiment using ^{13}C labeled model compounds to be converted as a consequence of the coupling of coniferyl alcohol radicals generated by the homolytic cleavage of the β-aryl ether linkage via a quinonemethide intermediate into a phenylcoumaran structure and others. hydrolysis of guaiacylglycerol-β-syringyl ether at low2) and high3) temperatures, and in 5% sulfuric acid-catalyzed reaction4) of syringylglycerol-β-syringyl ether at 100°C. Furthermore, the homolytic fragmentation5) of lignin macromolecules is thought to contribute to bulk delignification.

Phenylcoumaran and 1,2-diaryl-1,3-propanediol units also are important structural elements of lignin. Extensive studies on the reactivity of phenylcoumaran and 1,2-diaryl-1,3-propanediol units, under acidic conditions with dilute hydrochloric acid as in acidolysis, have been carried out by Adler and Lundquist. Adler and coworkers6),7) observed that phenylcoumaran was converted almost quantitatively into phenylcoumarone together with a minor stilbene derivative. This reaction is widely used for the determination8) of phenylcoumaran content in lignins. Furthermore, Lundquist7), 9), 10) was able to isolate a stilbene derivative and rearrangement compounds from acidolysis products of a model with 1,2-diarylpropanol unit. The stilbene derivatives were formed by loss of formaldehyde from their terminal side chains by a reversed Prins reaction.

In acidic media, these structural elements can be converted into their corresponding benzylium ions, formed by cleavage of an aryl ether bond and a hydroxyl group by the action of proton, which is conpetitively responsible for condensation reaction in addition to degradation reactions described above. In condensation11), 12), 13), position 6 of free and etherified guaiacyl nuclei, in other words para position of guaiacyl nuclei, have been found to be reactive. The present work deals with experiments illustrating degradation and condensation reactions of these structural elements during acetic acid cooking. Phenylcoumaran and 1,2-diarylpropanol contents14)in softwood lignin are only 0.14 and 0.15 per phenylpropane unit, respectively. Therefore, the behaviour of model compounds in acetic acid pulping is investigated in the presence of creosol as an aromatic nucleus model.

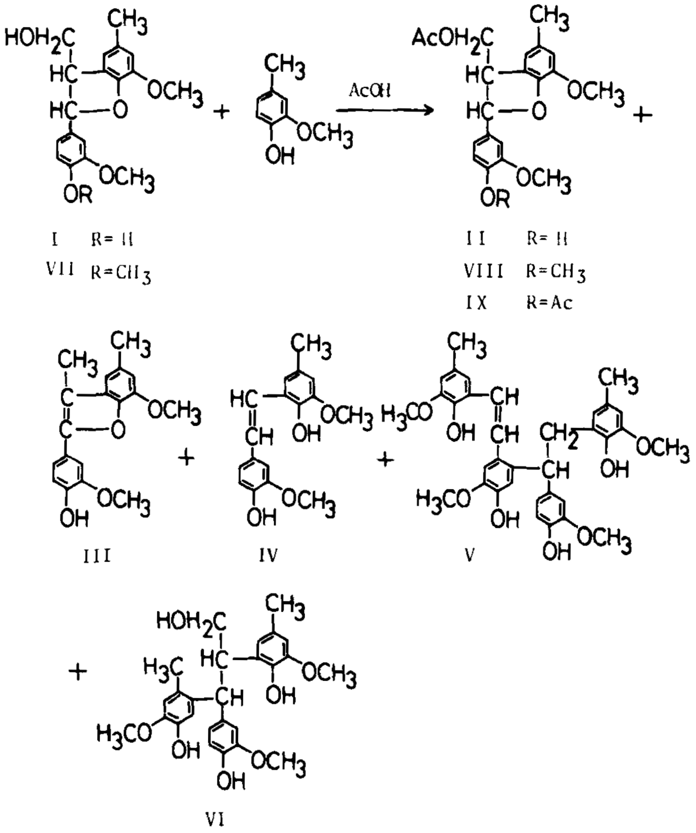

Figure 1. Reaction of phenylcoumaran in the presence of creosol in 90% acetic acid (AcOH) at 180°C.

RESULTS AND DISCUSSION

Phenylcoumaran

By the silica gel column chromatography of reaction products obtained by cooking the mixture of phenolic phenylcoumaran I and creosol as an aromatic nucleus model in 90% acetic acid for 3 hours, compounds II-VI as shown in Fig. 1 were isolated. Compound II is the acetylation product of the starting material. The facile acetylation[1)] of an alcoholic hydroxyl group under the

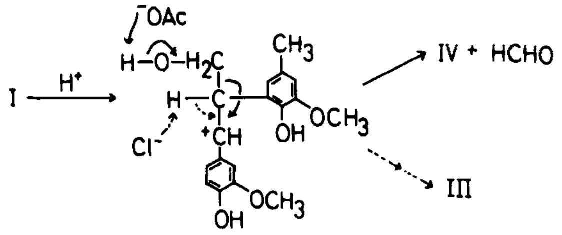

Figure 2. Reaction mechanism of I in acetic acid and in dilute hydrochloric acid.

conditions used has been demonstrated in acetic acid cooking of 1-guaiacyl-3-propanol and arylglycerol-β-aryl ether.

Compounds III and IV are phenylcoumarone and a stilbene derivative, respectively, well-known as acidolysis products of phenylcoumaran structure. The preferential formation of the stilbene derivative, in contrast to almost quantitative conversion15) of phenylcoumaran in hydrochloric acid-catalyzed acidolysis and alcoholysis into phenylcoumarone, may be interpreted in terms of deprotonation reaction of the bulky conjugate base (CH_3COO^-) of acetic acid. As shown in Fig. 2, chloride ion (Cl^-) in the acidolysis and alcoholysis mainly attacks on the sterically hindered β-hydrogen atom of an intermediate benzylium cation, yielding an unsaturated compound, which is then transformed into phenylcoumarone III. On the other hand, bulky conjugate bases (HSO_4^- and CH_3COO^-) of sulfuric acid and acetic acid, respectively, attack the terminal hydroxymethyl group of the cation, giving stilbene derivative IV. In this competitive reaction, formation of III is preferred to that of IV.

The characteristic absorption at 33.6 and 44.8 ppm in the ^{13}C NMR spectrum and the fragmentation pattern in the MS spectrum suggested that compound V has the condensed structure in Fig. 1. Compound VI should be formed by a condensation between the starting material and creosol. The lack of an acetyl group, which should be introduced in acetic acid cooking, may be due to

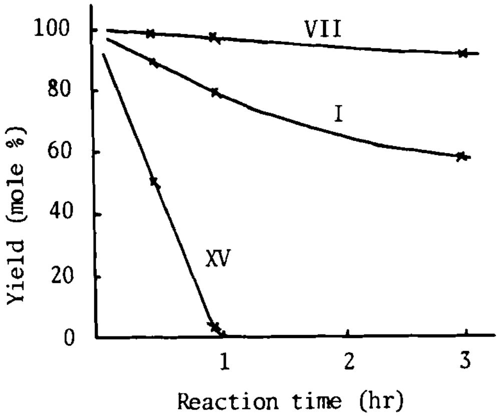

Figure 3. Consumption of model compounds (I, VII and XV) in acetic acid cooking. Remained model compounds were determined as their acetates after acetylation of the reaction mixture.

hydrolysis during silica gel chromatography. Very low yield (3%) of VI, in spite of three equivalents addition of creosol, can be explained by steric hindrance of the bulky aryl substituent at the β-position to nucleophilic attack of creosol in Fig. 2, and by the stability of the coumaran structure to a considerable extent.

From the reaction mixture prepared by a 3 hour cook of non-phenolic phenylcoumaran VII and creosol, only acetylated starting material VIII was isolated in a 76% yield. The high recovery of a phenylcoumaran skeleton up to 85% suggests the strong stability of the skeleton against acetic acid.

As shown in Fig. 3, even the consumption of the phenolic arylcoumaran model was very slow. This is in accordance with intense signals[1)] due to a phenylcoumaran structure in the ^{13}C NMR spectrum of 90% acetic acid-cooked products of ^{13}C labeled arylglycerol- β-aryl ether. In other words, homolytic cleavage of the β-aryl ether linkage leads to the formation of phenylcoumaran structure, which was almost unchanged in the reaction solution without further degradation.

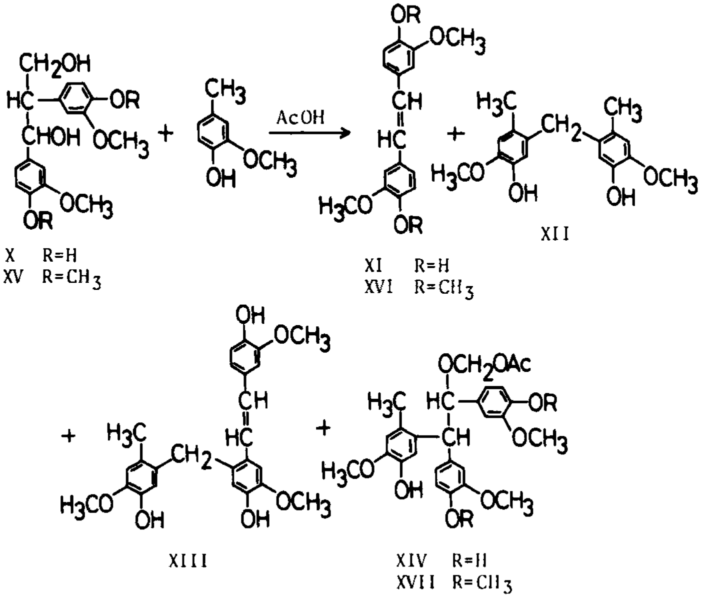

Figure 4. Reaction of 1,2-diaryl-1,3-propanediol in the presence of creosol in 90% acetic acid at 180°C.

1,2-Diaryl-1,3-propanediol

From the reaction mixture obtained by cooking phenolic model compound X and creosol in 90% acetic acid, four products XI-XIV were separated, as shown in Fig. 4. The formation of XI involves the elimination of the terminal hydroxymethyl group as formaldehyde. The liberated formaldehyde, as expected, undergoes acid-promoted condensation reactions with added creosol as an aromatic nucleus model and with degradation product XI, yielding XII and XIII. Although additional products of this reaction were not characterized, a condensation product composed of two molecules of XII must be formed.

Apparently, compound XIV is an intermolecular condensation product between the starting material and creosol. The low yield of XIV may be explained in the facile transformation of the benzylium cation, formed from the starting material by the loss of an α-hydroxyl group, into stilbene derivative XI and in low reactiviity of the sterically hindered cation toward a condensation reaction.

From the product mixture prepared by cooking non-phenolic model XV and creosol, only two compounds XVI and XII were isolated. The lack of absorptions in the ^{13}C NMR spectrum of the mixture near 48 ppm due to the α- and β-carbons of XVII suggests that only minor amounts of condensation products could be formed.

The consumed amount of the starting material in cooking liquor is shown in Fig. 3, indicating rapid degradation of non-phenolic 1,2-diaryl-1,3-propanediol model XV to the stilbene derivative with loss of the terminal hydroxymethyl group as formaldehyde.

In conclusion, results of lignin model compounds indicate the order of decreasing reactivity as follows: 1,2-diaryl-1,3-propanediol > arylglycerol- β-aryl ether > phenylcoumaran.

EXPERIMENTAL

Synthesis of model compounds

Phenylcoumarans I and VII, and 1,2-diaryl-1,3-propanediols X and XV were synthesized as described in previous papers16),17).

General procedure for isolation of acetic acid-cooked products of a model compound

A solution of 300 mg of a model dimer and about 390 mg (three equivalents to the model) of creosol in 6 ml of 90% acetic acid in a sealed glass tube was heated at 180°C for 3 hours. After cooling, the solution was diluted with water and extracted with ethyl acetate. The ethyl acetate layer was washed with water, dried over sodium sulfate and evaporated under reduced pressure.

(1) Phenolic phenylcoumaran I

The silica gel column chromatography of the reaction products, obtained by treating 198 mg of I and 260 mg of creosol, with mixed solvents of n-hexane and the increasing proportion of acetone as a eluent gave 104 mg (46.4%) of phenolic monoacetate II, 11 mg (5.9%) of phenylcoumarone III18), 31 mg (17.3%) of stilbene derivative IV19), 14 mg (9.4%) of V, 13 mg (6.6%) of starting material I and 8 mg (2.8%) of condensation product VI18). II; ^{13}C NMR δ: 20.9, 21.3, 50.7, 56.0, 65.6, 88.4, 108.2-146.7, 170.8. III18); ^{13}C NMR δ: 9.5, 21.7, 56.2, 108.8-151.8. IV19); ^{1}H NMR δ: 21.2, 56.2, 110.1-148.6. V; MS m/e: 572 (M^+), 421, 287, 151; ^{1}H NMR δ: 1.78 (3H, s), 2.13 (3H, s), 3.34 (2H, m), 3.55 (3H, s), 3.71 (3H, s), 3.75 (3H, s), 3.88 (3H, s), 4.30 (1H, m), 5.31 (1H, s), 5.37 (1H, s), 5.58 (2H, s), 6.10-6.70 (11H, m); ^{13}C NMR δ: 20.6, 21.1, 33.6, 44.8, 55.7, 108.8-145.6. VI18); ^{13}C NMR δ :19.5, 19.8, 21.3, 45.9, 46.4, 46.9, 56.1, 64.9, 110.6-148.0.

(2) Non-phenolic phenylcoumaran VII

The product mixture prepared by treating 240 mg of VII and 340 mg of creosol was chromatographed on silica gel using n-hexane-acetone (4:1 v/v) to separate 206 mg (76.1%) of monoacetate VIII and 31 mg (8.3%) of VII. VIII; ^{1}H NMR δ: 2.00 (3H, s), 2.30 (3H, s), 3.82 (10H, m), 4.34 (2H, m), 5.42 (1H, d, J=7 Hz), 6.56-7.00 (5H, m); ^{13}C NMR δ: 20.7, 21.3, 50.5, 55.8, 65.5, 88.1, 109.1-148.9, 170.6.

(3) Phenolic 1,2-diaryl-1,3-propanediol X

The product mixture prepared from 296 mg of X and 390 mg of creosol was chromatographed on silica gel with mixed solvents of n-hexane and increasing proportions of acetone to isolate 84 mg (33.4%) of XI20), 101 mg (37.9%) of XII1), 34 mg (8.7%) of XIII and 42 mg (9.4%) of XIV. XIII; MS m/e; 422 (M^+); ^{13}C NMR δ: 19.3, 35.3, 56.0, 107.8-145.2. XIV; ^{13}C NMR δ: 19.6, 20.8, 48.3, 48.7, 55.8, 67.8, 110.3-146.6, 170.8.

(4) Non-phenolic 1,2-diaryl-1,3-propanediol XV

The silica gel column chromatography of the reaction products, obtained by treating 131 mg of XV and 170 mg of creosol, using n-hexane-acetone (4:1) gave 46 mg (40.7%) of XVI and 67 mg (61.8%) of XII.

Determination of consumed amount of starting material in cooking liquor

A solution of 20 mg of a model compound and 28 mg of creosol in 0.75 ml of 90% acetic acid was treated in a sealed glass tube at 180°C (oil bath temperature) for desired periods of time. After quenching by immersion of the sealed tube in water, each reaction solution was diluted with water and extracted with ethyl acetate. Each ethyl acetate layer was washed with water, dried over sodium sulfate and then evaporated under reduced pressure. The residue was then acetylated with acetic anhydride and pyridine in the usual manner. The acetylated products were analyzed by gas liquid chromatography under the following conditions; Column: 2% Silicone OV-1 on Chromosorb W (AW-DMCS; 100-120 mesh) in a stainless steel 2 m; carrier gas: nitrogen at 15 ml/min.; temperature: 250°C; detector: flame ionization detector (FID).

Measurement

The ^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ on a JEOL JNM-MH-100 NMR spectrometer. TMS was employed as an internal reference.

REFERENCES

1) S. Yasuda and N. Ito, Mokuzai Gakkaishi, 33, 708(1987).

2) H. Nimz, U. Tschirner and M. Roth, Procedings of 1983 International Symposium on Wood and Pulping Chemistry, Tsukuba, Volume 1, p.90(1983) and an additional supplement paper.

3) Y. Sano, Mokuzai Gakkaishi, 21, 508(1975).

4) S. Yasuda and K. Ota, Holzforschung, 41, 59(1987).

5) T. K. Kleinert, Papier, 21, 653(1967).

6) E. Adler, S. Delin and K. Lundquist, Acta Chem. Scand., 13, 2149(1959).

7) E. Adler, K. Lundquist and G. E. Miksche, Adv. Chem. Ser., 59, 22(1966),

8) E. Adler and K. Lundquist, Acta Chem. Scand., 17, 13(1963).

9) K. Lundquist and G. E. Miksche, Tetrahedron Letters, 2131(1965).

10) K. Lundquist, Acta Chem. Scand, 24, 889(1970)

11) J. C. Pew, J. Am. Chem. Soc., 73, 1678(1951); 74, 2850(1952).

12) J. M. Harkin, Adv. Chem Ser., 59, 65(1966).

13) S. Yasuda and K. Ota, Mokuzai Gakkaishi, 32, 51(1986).

14) K. V. Sarkanen and C. H. Ludwig, Lignins, p.226-228, Wiley-Interscience, New York, 1971.

15) E. Adler, S. Delin and K. Lundquist, Acta Chem. Scand., 13, 2149(1959).

16) S. Yasuda, K. Ota and T. Hirano, Mokuzai Gakkaishi, 32, 915(1986).

17) S. Yasuda, Mokuzai Gakkaishi, 31, 119(1985).

18) S. Yasuda, Mokuzai Gakkaishi, 30, 166(1984).

19) B-H. Yoon, N. Terashima and S. Yasuda, Mokuzai Gakkaishi, 27, 311(1981).

20) S. Yasuda, K. Adachi, N. Terashima and K. Ota, Mokuzai Gakkaishi, 31, 125(1985) and references therein.