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Acid Degradation of Lignin

III.* Formation of Formaldehyde

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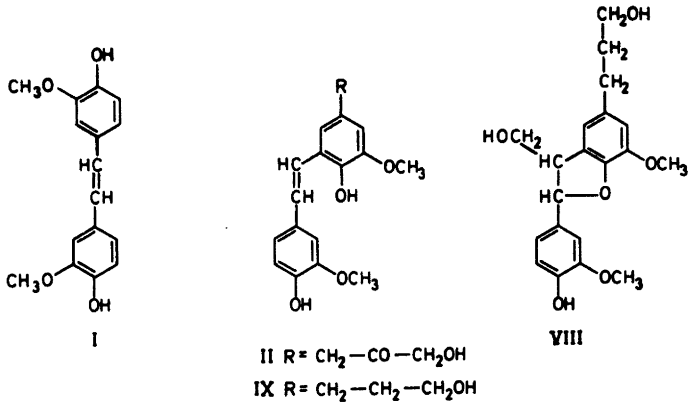
The liberation of formaldehyde from spruce lignin and lignin model compounds on 4 h refluxing with 0.2 M HCl in dioxane-water (9:1) has been studied. The results indicate that the formaldehyde produced from lignin on this treatment arises primarily from structural elements of the arylglycerol-β-aryl ether, phenylcoumaran, and 1,2-diaryl-1,3-propanediol types. Some of the low molecular weight phenolic products present in the lignin acidolysis mixture are considered to be formed in reactions involving a release of formaldehyde; these products include stilbenes I and II, and homovanillin (III). The detection of compound III is described in the present paper.

It is well-known that formaldehyde is liberated on acid treatment of lignin. From experiments with 28 % sulphuric acid as reagent, Freudenberg and co-workers (see Ref. 1) concluded that the formaldehyde arises from terminal hydroxymethyl groups in the side chains of phenylpropane units. Some of the compounds [2] in the reaction mixture obtained from Björkman lignin from spruce on heating with 0.2 M HCl in dioxane-water (9:1) at reflux temperature** for 4 h can be considered to be formed in reactions involving such a release of formaldehyde from hydroxymethyl groups. These products include the stilbenes I and II; stilbene I is assumed to originate from 1,2-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol incorporated in the lignin,[3] and stilbene II from structural elements of the phenylcoumaran type, carrying a glycerol side chain to which an adjacent unit is linked by a β-aryl ether bond.[2]

A third component of the lignin acidolysis mixture, homovanillin (III), the detection of which is described in the present paper, is also thought to arise in connection with the formation of formaldehyde. The homovanillin is presumed to originate from structural elements of the guaiacylglycerol-β-aryl ether type. This assumption is supported by the fact that homovanillin

* Part II, see Ref. 2.

** Throughout this paper the term "acidolysis" is used specifically for this treatment.



also is present in the reaction mixture obtained on 4 h acidolysis of a model compound representative of this type of structure, *viz.* guaiacylglycerol-*β*-(2-methoxyphenyl)-ether (IV).

A proposed reaction route for the formation of homovanillin from compound IV is shown in Fig. 1. An equilibrium between compound IV and the benzylium ion V is established in the acidolysis mixture. Compound IV decomposes *via* the benzylium ion V, with loss of water, to the enol ether VI and formaldehyde. (The formation of stilbenes I and II from structural elements in lignin is similarly considered to proceed *via* benzylium ions in an analogous way.[3,4] This type of reaction can be regarded as a reverse Prins reaction.) The enol ether (VI) then undergoes hydrolysis to yield homovanillin (III) and guaiacol. Support for this second step was provided in an acidolysis

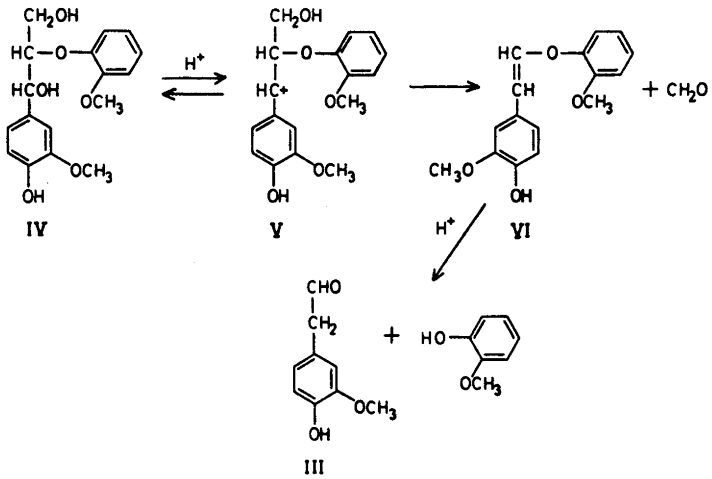


Fig. 1. Reaction route for the formation of homovanillin (III) from guaiacylglycerol-*β*-(2-methoxyphenyl)-ether (IV) on acidolysis.

experiment with the enol ether VI; brief acidolysis (5 min) of this compound resulted in the formation of homovanillin and guaiacol. It has previously been reported (Ref. 5, see also Ref. 6) that compound VI decomposes under acid conditions and that guaiacol and a carbonyl compound were present in the reaction mixture.

To elucidate the connection between reactions involved in formation of compounds I – III and the origin of the formaldehyde, the liberation of formaldehyde from some appropriate lignin model compounds as well as lignin on 4 h acidolysis was studied.

From guaiacylglycerol-β-(2-methoxyphenyl)-ether (IV) formaldehyde was obtained in a 3 % yield; the yield of homovanillin (III) was of the same order, which is in accord with the suggested reaction route (Fig. 1). The major components of the 4 h acidolysis mixture obtained from compound IV are ketol VII and guaiacol.[7] Acidolysis of ketol VII gave no formaldehyde, showing that formaldehyde from compound IV had not been formed *via* ketol VII.

A model compound of the phenylcoumaran type, dihydrodehydrodiconiferyl alcohol (VIII), gave formaldehyde in 9 % yield. Stilbene IX, considered to be formed in connection with a release of formaldehyde, has been detected in the reaction mixture.[8] (This compound has previously been obtained in high yield from compound VIII by treatment under "kraft cooking" conditios.[9]) The stilbene was a minor component and its yield appeared to be about the same as that of formaldehyde. The predominating component of the acidolysis product obtained from compound VIII is a phenylcoumarone.[10]

A third model compound, 1,2-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol, yielded 15 % formaldehyde on acidolysis. In this case also, there was a reasonable agreement between the yield of formaldehyde and the yield of the compound considered to be formed in connection with liberation of formaldehyde, *i.e.* stilbene I.[3]

VII	$R-CH_2-CO-CH_2OH$
X	$R-CH=CH-CH_2OH$
XI	$R-CHO$
XII	$R-CH_2-CH_2OH$
XIII	$R'-CH_2-CH_2-OCOCH_3$
XIV	$R'-CH_2-OCOCH_3$

R = 4-hydroxy-3-methoxyphenyl

R′ = 4-acetoxy-3-methoxyphenyl

Experiments with the derivatives obtained from the above-mentioned model compounds by methylation of the phenolic hydroxyl groups showed essentially the same picture as the corresponding non-methylated compounds with respect to formaldehyde formation.

Coniferyl alcohol (X), which is considered to be linked to lignin as end groups, yielded a small amount of formaldehyde (0.7 %).

Neither (+)-pinoresinol nor its dimethyl ether gave formaldehyde under acidolysis conditions.

From Björkman lignin of spruce the yield of formaldehyde on 4 h acidolysis was 2–3 % (calculated per methoxyl group), when the concentration of sample in the acidolysis mixture was of the same order as in the experiments with model compounds, *i.e.* about 0.5 %. With lignin concentrations of 1 %, 2 %, and 4 %, the yield was 1.1 %, 0.6 %, and 0.4 %, respectively. It is therefore clear that an increase in the lignin concentration causes a decrease in the yield of formaldehyde. A plausible explanation is that formaldehyde liberated is consumed to a larger extent by reactions with the lignin when the concentration of the latter is increased. It seems likely that the consumption is due to condensation reactions leading to diphenylmethane structures. Variation of the yield of formaldehyde with concentration may also occur in the experiments with lignin model compounds; this has, however, not been investigated.

On the basis of the results described above and considering what is known about the frequency of different structural elements in lignin (see, *e.g.*, Refs. 4 and 1), it seems reasonable to conclude that the formaldehyde obtained from lignin arises primarily from structural elements of the arylglycerol-β-aryl ether, phenylcoumaran, and 1,2-diaryl-1,3-propanediol types.

The formaldehyde was determined by colorimetry using the chromotropic acid method. In addition to the absorption caused by formaldehyde the measuring solutions obtained from lignin acidolysis exhibited an absorption maximum around 397 nm. This is due to the presence of pyruvaldehyde,[11] which has previously been detected [12] in the lignin acidolysis mixture.

Experiments with synthetic mixtures of pyruvaldehyde and formaldehyde indicated that when substantial amounts of pyruvaldehyde were present, the determined formaldehyde values were too low. This effect could conceivably have been of importance in the experiments with a 4 % lignin concentration, in which case the absorption due to pyruvaldehyde was relatively strong compared to that due to formaldehyde. However, in repeated experiments with this lignin concentration, separation of formaldehyde and pyruvaldehyde by ion exchange chromatography [13] and subsequent determination of formaldehyde gave results which did not differ significantly from those obtained with the original mixtures.

It is noteworthy that neither the model compounds examined nor borohydride-reduced lignin gave rise to any absorption at 397 nm. This provides further support for the earlier proposal [12] that the pyruvaldehyde originates from glyceraldehyde-2-aryl ether structures.

EXPERIMENTAL

Paper chromatography was performed using the solvent system toluene-acetic acid-water (4:1:5) (descending, upper layer mobile phase). Paper: Schleicher & Schüll 2043 b Mgl. Temperature: 22°. Diazotized sulphanilic acid in 10 % aqueous Na_2CO_3 was used as detecting agent. R_F values: homovanillin (III), 0.50 (red-violet); vanillin (XI), 0.74 (orange).

Thin layer chromatography was carried out on silica gel (Merck G) plates with benzene-ethyl acetate (4:1) as eluent. R_F values: 2-(4-hydroxy-3-methoxyphenyl)-ethanol (XII), 0.10; vanillin (XI), 0.30 (dependent on the amount of the compound); homovanillin (III), 0.35; guaiacol, 0.50. Compounds were made visible as brown spots by exposure to iodine vapour. Homovanillin and vanillin gave yellow and orange spots, respectively, on spraying with 2,4-dinitrophenylhydrazine in dilute hydrochloric acid.

For *gas chromatography* a Perkin-Elmer Model 880 instrument was used. Column dimensions: 100 × 0.3 cm stainless steel tubing. Solid support: Chromosorb G, acid-washed and treated with dimethyldichlorosilane, 80—100 mesh. Stationary phase: Silicone elastomer SE-30, General Electric (1 % by weight of solid support), and Carbowax 20 M terminated with terephthalic acid (0.2 % by weight of solid support). Temperatures: injection 260°, detector 210° and column 190°. Carrier gas: N_2, 30 ml/min. Detector: flame ionization.

Preparation of diacetate XIII. 2-(4-Hydroxy-3-methoxyphenyl)-ethanol (XII) with a m.p. of 41—43° (Lit.[14] 43—44°) was treated with acetic anhydride-pyridine at room temperature for 24 h. Distillation (1 mmHg, 120° bath temperature) of the crude product obtained on evaporation of excess reagents gave a colourless oil. (Found: C 61.61; H 6.31. Calc. for $C_{13}H_{16}O_5$: C 61.89; H 6.39.) The NMR spectrum, recorded on a Varian A-60 instrument with deuterochloroform as solvent and TMS as internal standard, was consistent with structure XIII. Singlets at $\delta = 2.00$ (3H) and $\delta = 2.26$ (3H) are assigned to the methyl protons in the acetoxy group in the side chain and the acetoxy group on the aromatic ring, respectively.

Conversion of homovanilllin (III) to diacetate XIII. Homovanillin was dissolved in a saturated solution of $LiBH_4$ in ether (more than ten-fold excess $LiBH_4$). After 2 h the reaction mixture was acidified by addition of dilute hydrochloric acid and extracted with chloroform. The extract was dried over anhydrous Na_2SO_4 and solvent removed by film evaporation. As indicated by thin layer chromatography, the residue obtained consisted of 2-(4-hydroxy-3-methoxyphenyl)-ethanol (XII). Acetylation with acetic anhydride-pyridine gave a product identified as compound XIII by gas chromatography.

Detection of homovanillin (III) in the acidolysis mixtures from lignin and compound IV. The separation of a fraction containing homovanillin as a component from the reaction mixture obtained on 4 h acidolysis of Björkman lignin from spruce is described in Ref. 2. A corresponding fraction, which was about 3 % of the starting material, was prepared in a similar way from the product obtained on 4 h acidolysis of guaiacylglycerol-β-(2-methoxyphenyl)-ether (IV). Homovanillin and vanillin were detected in both fractions by paper chromatography and thin layer chromatography. In addition, a trace of *p*-coumaraldehyde in the fraction from lignin was indicated by paper chromatography.[2] The fractions were reduced and acetylated as described above to convert homovanillin to derivative XIII. The presence of compound XIII in the products obtained was indicated by gas chromatography (retention time 4 min) and was confirmed by mass spectrometry, using an LKB 9000 gas chromatograph-mass spectrometer unit. The gas chromatograms showed a second peak (retention time 3 min), which was due to the presence of the diacetate XIV, which is produced from vanillin on reduction-acetylation.

Acidolysis and determination of formaldehyde liberated. Samples (20—200 mg in the case of lignin (Björkman lignin from spruce, methoxyl content 15.6 %), 10—30 mg in case of model compounds) were dissolved in 5 ml 0.2 M HCl in dioxane-water (9:1). The solutions in sealed glass ampoules were kept for 4 h in refluxing acidolysis reagent. After being cooled, the ampoules were opened and the contents transferred to a separatory funnel (the transfer was made complete with help of some water). The reaction mixture was neutralized with 5 ml 0.2 M aqueous $NaHCO_3$ and extracted with 5 ml, and then with 2 × 2.5 ml chloroform. To separate the formaldehyde, the aqueous layer (about 10 ml) was distilled. When a few ml remained, 2 ml water was added, and distilling was then continued until the total distillate was about 9 ml. The distillate was diluted to 10 ml in a volumetric flask, and formaldehyde determined by the chromotropic acid method according to Ref. 15. By examining solutions of known amounts of formaldehyde in the acidolysis reagent it was found that losses in the described work-up procedure were about 10 %. Although the dioxane used was purified first according to Ref. 16, and subsequently according to Ref. 17, some formaldehyde appeared to be formed from the dioxane during the acidolysis (about 0.002 mg/ml). The formaldehyde yields given have not been corrected for losses in the work-up procedure or for formaldehyde liberated from the dioxane.

Acidolysis of enol ether VI. A sample of the sodium salt of compound VI [5] (30 mg) was dissolved in 5 ml 0.2 M HCl in dioxane-water (9:1). The solution was refluxed for 5 min. After neutralization with 5 ml 0.2 M aqueous $NaHCO_3$, the reaction mixture was extracted with chloroform. The chloroform extract was dried over anhydrous Na_2SO_4 and solvent removed by film evaporation. Examination of the residue by thin layer chro-

matography indicated the presence of homovanillin (III) and guaiacol, and further proof for the presence of homovanillin was provided by paper chromatography.

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