

1. Karlén, B. and Bogentoft, C. *Acta Pharm. Suecica* **6** (1969) 543.
2. Brant, R. and Djerassi, C. *Helv. Chim. Acta* **51** (1968) 1750.
3. Wolff, R. E., Greff, M. and McCloskey, J. A. *Advan. Mass Spectrom.* **4** (1968) 193.
4. Williams, D. H. and Cooks, R. G. *Chem. Commun.* **1968** 663.
5. Waters, J. and Wiese, G. A. *J. Am. Pharm. Assoc.* **49** (1960) 112.

Received January 27, 1971.

## Acid Degradation of Lignin

### VI.\* Formation of Methanol\*\*

KNUT LUNDQUIST and  
LENNART ERICSSON

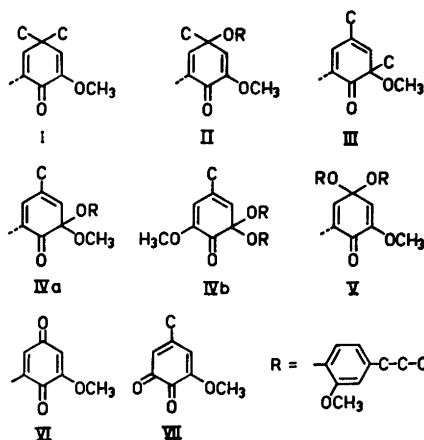
Department of Organic Chemistry, Chalmers  
University of Technology and University of  
Göteborg, Fack, S-402 20 Göteborg 5,  
Sweden

In a previous paper<sup>1</sup> the possibility was considered that cyclohexadienone structures of type I, produced *via* an oxidative phenol coupling, occurred in lignin. Structures II–V constitute some other types of dienone units which conceivably also could arise during the oxidative coupling of phenols involved in the biosynthesis of lignin.<sup>2,3</sup> From the suggested structural elements of the quinone ketal type (IV and V) quinone units may be formed. Thus, hydrolysis of *o*-quinone ketals (IV) with formation of *o*-quinone units of type VII may occur in the plant. Analogously, *p*-quinone units of type VI may arise by hydrolysis of *p*-quinone ketals (V) (see Ref. 4). Alternatively, *p*-quinone units could be thought to be formed in connection with an oxidative elimination of a propyl side chain (Ref. 5, *cf.* also Ref. 6).

In preliminary experiments it was found that methanol was liberated when lignin samples, as well as model compounds for structures II–VII, were subjected to

\* Part V, *Acta Chem. Scand. In press.*

\*\* The major part of this work was presented at "Det 13. Nordiske Kemikermøde", Copenhagen, 19–23 August 1968.



acidolysis by heating with 0.2 M hydrogen chloride in dioxane-water (9:1) at reflux temperature\* (concerning the formation of methanol from compounds related to structures III and V on acidic treatment, see Refs. 7, 2, and 4). Evidently the methanol originated from methoxyl groups. In the present work, formation of methanol from lignin and lignin model compounds on acidolysis was studied in order to clarify whether quinonoid and quinone units of types II–VII may occur in lignin. The methanol was determined by gas chromatography.

The amounts of methanol obtained on acidolysis of spruce lignin (Björkman lignin from *Picea abies*) were relatively small; on prolonged treatment the yield was about 0.02 mol/OCH<sub>3</sub> (Table 1). Similar results were obtained with a lignin sample which, to avoid contact with acid, had been purified according to a procedure which differed somewhat from that used by Björkman<sup>8</sup> (the precipitation from 90% acetic acid into water was replaced by precipitation into 1% aqueous sodium sulphate solution from a dioxane-water (19:1) solution), but an observed difference was that traces of methanol ( $\approx 0.001$  mol/OCH<sub>3</sub>) were liberated even at room temperature on brief treatment (0.25 h) with the acidolysis reagent. A hardwood lignin (Björkman lignin from *Betula verrucosa*) gave a somewhat higher yield of methanol than spruce lignin on 4 h acidolysis (Table 1).

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

Table 1. Yields of methanol on acidolysis.

Sample <sup>a</sup>	Time of acidolysis (h)				
	0.25	1	4	8	24
VIII <sup>b</sup>	0.28		0.47		
IX <sup>b</sup>	0.08		0.30		0.70
X <sup>b</sup>	1.9				
XI <sup>b</sup>	0.05		0.55		0.65
Spruce lignin <sup>c</sup>	0.006	0.014	0.018		0.02
Birch lignin <sup>c</sup>			0.03		
Birch xylan <sup>c</sup>	0.003	0.03	0.25		
2-O-(4-O-Me- $\alpha$ -D-GpA)-D-Xyl <sup>b</sup>	0.004	0.02	0.26	0.45	
4-O-Methyl-D-glucuronic acid <sup>b</sup>	0.15	0.64	0.77	0.42	

<sup>a</sup>Gifts of compounds from Prof. E. Adler and Fil.lic. G. Andersson (compounds X and XI), Dr. H. D. Becker (compound VIII), Prof. O. Samuelson (uronic acids) and Laborator O. Theander (birch xylan) are gratefully acknowledged.

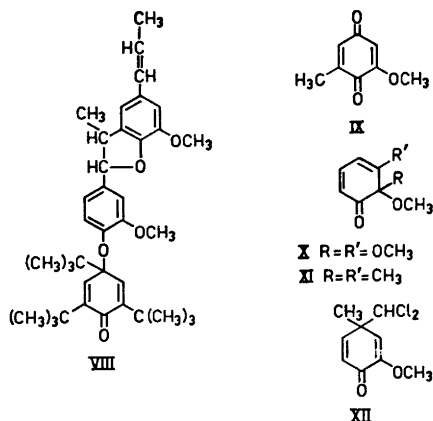
<sup>b</sup>Yields given in mol/mol.

<sup>c</sup>Yields given in mol/OCH<sub>3</sub>.

Model compounds for structural elements of types II, III, IVa, VI, and VII gave varying but in general substantial amounts of methanol on acidolysis. Results obtained with some of the model compounds investigated are given in Table 1. The dioxepin \* obtained by Pew and Connors<sup>4</sup> on enzymatic oxidation of (4-hydroxy-3-methoxyphenyl)-1-propanol also was examined. This dioxepin contains a *p*-quinone ketal grouping as in structure V, and can therefore be considered as a

model compound for this type of structure. The yield of methanol was about 0.9 mol/mol on acidolysis for periods of time varying between 0.25 h and 4 h. Formation of methanol on acid treatment of this compound has previously been encountered.<sup>4</sup> Compound XII<sup>5</sup> which was used as a model compound for dienone structures of type I gave no methanol on acidolysis.

A variety of lignin model compounds representative of the major kinds of units in lignin also was examined. These compounds, in contrast to the quinonoid compounds and quinones discussed above, merely contain methoxyl groups linked to aromatic rings. All the compounds of this type investigated gave <0.001 mol/mol methanol on brief acidolysis (0.25 h) and most of them (guaiacol, vanillin, vanillic acid, 3,4-dimethoxybenzaldehyde, coniferaldehyde, syringaldehyde, 2,6-dimethoxyphenol, guaiacylglycerol- $\beta$ -(2-methoxyphenyl) ether, veratrylglycerol- $\beta$ -(2-methoxyphenyl) ether, dihydrodehydrodiconiferyl alcohol, (+)-pinoresinol) gave none or negligible amounts (<0.001 mol/mol) even on acidolysis for 4 h. However, a few of the compounds examined gave higher yields of methanol on 4 h acidolysis. Thus 1,2-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol and a compound of the biphenyl type, 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl, gave about 0.005 mol/mol. A greater amount of methanol was obtained from a second compound of the biphenyl



\* The authors thank Dr. J. C. Pew for a sample of this compound.

type, 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dipropylbiphenyl, which gave 0.02 mol/mol on 4 h acidolysis.

According to the results obtained from experiments with quinonoid compounds and quinones, the methanol liberated on acidolysis of lignin may originate from minor amounts of structural elements of types II–VII present in the lignin. The acidolysis experiments with model compounds representative of the major part of the units in lignin support this interpretation of the results, because most of the compounds of this type examined did not yield any appreciable amounts of methanol, and none of them gave a greater yield of methanol than obtained from lignin.

Björkman lignin preparations contain minor amounts of carbohydrates.<sup>9,10</sup> To investigate the possible contribution of methanol from 4-*O*-methyl-D-glucuronic acid units attached to the carbohydrates, the formation of methanol on acidolysis of 4-*O*-methyl-D-glucuronic acid, 2-*O*-(4-*O*-methyl- $\alpha$ -D-glucopyranosyluronic acid)-D-xylose, and a birch xylan was studied. As shown in Table 1 considerable amounts of methanol are liberated; probably because an initial hydrolysis to get free 4-*O*-methyl-D-glucuronic acid is required, only small amounts of methanol were obtained from 2-*O*-(4-*O*-Me- $\alpha$ -D-GpA)-D-Xyl and birch xylan on brief acidolysis. The number of 4-*O*-methyl-D-glucuronic acid units in Björkman lignin preparations can be expected to be rather small,<sup>9,10,11</sup> and therefore to give rise only to a minor portion of the methanol liberated on acidolysis.

*Experimental. Acidolysis.* The samples (5–40 mg) were heated for the desired periods of time with 1 ml 0.2 M HCl in dioxane-water (9:1) (the dioxane used was purified according to Ref. 12) in sealed glass ampoules with refluxing acidolysis reagent as heating bath. After being cooled, the ampoules were opened and 0.25 ml 1.2 M aqueous sodium acetate solution added. The mixtures were then analysed for methanol as described below. *Determination of methanol.* The samples were analysed for methanol by gas chromatography on a Perkin Elmer model 800 instrument equipped with a pre-injector

(see Ref. 13). *Method A.* Methanol was determined as described in Ref. 13. *Method B.* For the analysis a Porapak-Q column was used. Column dimensions: 100  $\times$  0.3 cm o.d. stainless steel tubing. *Temperatures:* Injection 150°, column 110°, detector 150°. *Carrier gas:* N<sub>2</sub>, 30 ml/min. 2,2,2-Trifluoroethanol was used as internal standard. In all acidolysis experiments methanol was determined according to method A and in most cases also according to method B.

*Acknowledgements.* The authors thank Prof. E. Adler for his kind interest in this work. Financial support from *Cellulosaindustriens stiftelse för teknisk och skoglig forskning samt utbildning* is gratefully acknowledged.

1. Lundquist, K. and Miksche, G. E. *Tetrahedron Letters* **1965** 2131.
2. Harkin, J. M. In Taylor, W. I. and Battersby, A. R. *Oxidative Coupling of Phenols*, Marcel Dekker Inc., New York 1967, p. 243.
3. Freudenberg, K. In Freudenberg, K. and Neish, A. C. *Constitution and Biosynthesis of Lignin*, Springer, Berlin 1968, p. 45.
4. Pew, J. C. and Connors, W. J. *J. Org. Chem.* **34** (1969) 580.
5. Kirk, T. K., Harkin, J. M. and Cowling, E. B. *Biochim. Biophys. Acta* **165** (1968) 145.
6. Adler, E. and Lundquist, K. *Acta Chem. Scand.* **15** (1961) 223.
7. Hewgill, F. R. and Middleton, B. S. *J. Chem. Soc. C* **1967** 2316.
8. Björkman, A. *Svensk Papperstid.* **59** (1956) 477.
9. Miksche, G. E. *Unpublished results.*
10. Björkman, A. and Person, B. *Svensk Papperstid.* **60** (1957) 158.
11. Timell, T. E. *Advan. Carbohydrate Chem.* **19** (1964) 247; **20** (1965) 409.
12. Vogel, A. I. *Practical Organic Chemistry*, 3rd Ed., Wiley, New York 1966.
13. Adler, E., Miksche, G. E. and Johansson, B. *Holzforschung* **22** (1968) 171.

Received January 26, 1971.