

Acidolytic Formation of Methanol from Quinones and Quinonoid Compounds Related to Lignin

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Quinone and quinonoid units may be important chromophoric groups in lignin.¹⁻³ In a previous paper, support for the presence of quinone and quinonoid units in lignin was given by the formation of methanol during acidolysis [heating with 0.2 M HCl in dioxan-water (9:1) at reflux temperature] of lignin and model compounds.⁴ In this report, additional results obtained by studies of the formation of methanol on acidolysis are presented. Acidolysis and determination of methanol was made as described in Ref. 4.

Results obtained with a number of quinones and quinonoid compounds are summarized in Table 1. The formation of

However, other routes, *e.g.* via an *o*-diphenoquinone (*cf.* Ref. 6), also seem possible. In the course of the examination of model compounds representative of major lignin structures (which merely contain methoxyl groups linked to aromatic rings) it was found that model compounds of the biphenyl type gave small amounts of methanol on acidolysis.⁴ Further studies showed that clearly larger amounts of methanol were obtained from biphenyl model compounds prepared by dehydrogenation of phenols, if the biphenyls were not carefully purified. It therefore seems possible that methanol obtained from model compounds of the biphenyl type is produced from contaminants with structural resemblance to compound I.

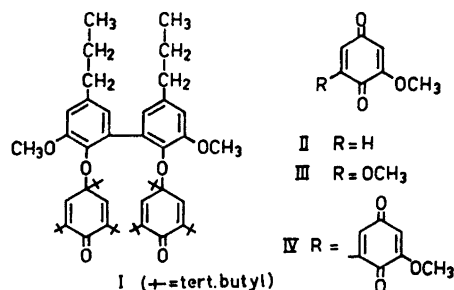
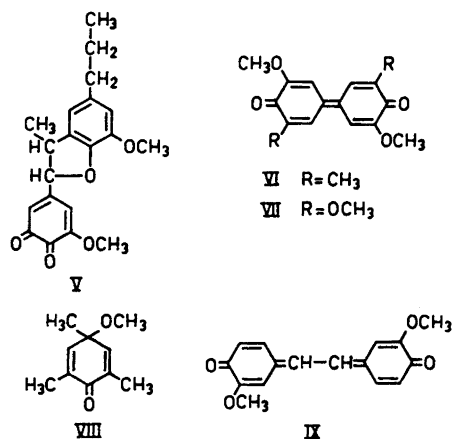


Table 1. Yields of methanol on acidolysis (given in mol/mol).

Compound ^a	Time of acidolysis (h)	
	0.25	4
I	0.66	0.81
II	0.02	0.08
III	0.16	1.7
IV	0.12	0.80
V	0.22	0.34
VI	1.0	—
VII	1.7	—
VIII	0.9	—
IX	0.00	0.00

^a Gifts of compounds from Prof. E. Adler (compound VIII) and from Dr. H.-D. Becker (compounds I, VI and IX) are gratefully acknowledged.

methanol from compound I may occur in analogy with the reaction route suggested by Hewgill and Middleton⁵ for the formation of methanol from a methoxyl containing *p*-quinol ether on acid treatment.



Compounds of the same type as compound I (aromatic *p*-quinol ethers) have been found to be in equilibrium with free radicals.⁷ Thus there may be a connection between the fact that various lignin prep-

arations have been found to contain minor amounts of free radicals⁹ and the occurrence of quinonoid structures in lignin.

The formation of methanol from methoxyquinones II–VII (concerning the preparation of IV and V, see Ref. 9) can be understood as a hydrolysis of vinylogous esters. The occurrence of lignin structures corresponding to compounds VI and VII, *i.e.* *p*-diphenoquinone structures, does not seem very likely. However, in recent studies on enzymatic oxidation of lignin model compounds a product has been obtained which possibly is a *p*-quinol ether on acidolysis.² The formation of methanol from compound VIII does not directly apply to formation of methanol from lignin, since methoxyl groups cannot be expected to be linked to lignin units in this position. However, the reaction is of interest as an example of a hydrolysis of a *p*-quinol ether on acidolysis. Although the stilbenequinone IX can be considered as an extended vinylogous ester, no methanol was formed on acidolysis. Possibly this compound, containing "quinone methide groupings" reacts under addition of water to these groupings. Stilbenequinone structures are not expected to occur in native lignin, but may occur in lignin preparations obtained on various hydrolytic treatments of lignin (*e.g.* kraft cooking) due to autoxidation of stilbene structures formed during the hydrolysis.

Relatively larger amounts of methanol were obtained from wood meal and lignin carbohydrate complex¹⁰ from spruce (about 0.05 mol/OCH₃ on 4 h acidolysis) than from Björkman lignin from spruce (0.018 mol/OCH₃ on 4 h acidolysis⁴). It is unclear if this result reflects a difference in content of quinone and quinonoid units, since 4-*O*-methylglucuronic acid units can be expected to give rise to a substantial portion of the methanol obtained from wood meal and lignin carbohydrate complex (see Ref. 4).

The formation of methanol from borohydride treated lignin was studied in connection with attempts to characterize quinone and quinonoid units in Björkman lignin from spruce. Methanol was formed but experimental difficulties did not permit any closer quantitative evaluation of the results. However, it appeared that some groups were formed on borohydride reduction which very rapidly gave methanol on acidolysis. Analogy with this behaviour was found in experiments with model compounds. The *o*-quinol ether model 6-

methoxy-5,6-dimethyl-2,4-cyclohexadienone has been found to give methanol slowly on acidolysis;⁴ however, after borohydride reduction, the reduced product rapidly gave high yield of methanol on acidolysis.

Treatment of lignin in dioxan-water solution with sulphur dioxide decreases the absorbance in the ultraviolet and the visible range. With methoxy-*p*-benzoquinone as reference compound ($\lambda_{\max} = 359$ nm, ϵ 1450) the decrease in absorbance corresponded to 1–2% units of quinone type of the total number of units. The decrease in absorption caused by sulphur dioxide treatment was only about 10% of the decrease caused by borohydride reduction.

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