Tetrahedron Letters No. 42 pp 3631 - 3634, 1975. Pergamon Press. Printed in Great Britain.

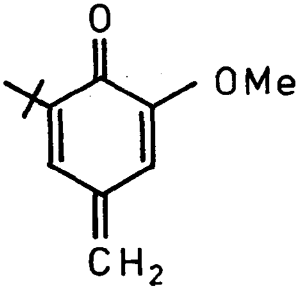
REACTIVE LIGNIN INTERMEDIATES (III): COMPETITIVE ADDITION OF SIMPLE HYDROXY COMPOUNDS AND THEIR CONJUGATE BASES TO A QUINONE METHIDE

Gordon Leary and Wayne Thomas
Chemistry Division, DSIR,
Private Bag, Petone, New Zealand.

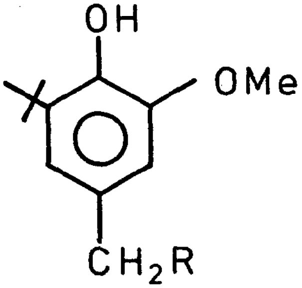
(Received in UK 2nd September 1975; accepted for publication 4th September 1975)

It is generally believed that lignin is covalently bonded to carbohydrates in wood. The nature of the bond has been the subject of much speculation and investigation, but a favoured suggestion is that lignin-carbohydrate links are formed by the addition of carbohydrate hydroxyl substituents to lignin quinone methides[1].

During lignification a number of hydroxy compounds (e.g. carbohydrates, carbohydrate uronic acids and water) are present. These may compete for addition to a quinone methide forming esters, ethers or alcohols. To try to determine which type of lignin-carbohydrate bonds may be favoured we have examined the products formed when quinone methide (I) is added to mixtures of simple hydroxy compounds, and to mixtures containing their conjugate bases.



(I)



(II)

Competitive Addition of Hydroxylic Solvents

A solution of the quinone methide was prepared by shaking a 10mM solution of the phenol (II,R=H)[2] in benzene with an excess of alkaline potassium ferricyanide solution. The organic phase (10 ml) containing quinone methide was then added to a range of equimolar (0.5 moles each) mixtures of two or more of the hydroxy compounds; water, ethanol, isopropanol and acetic acid. After 24 hours the solvents were removed by evaporation and the product ratios of the respective TMS ethers determined by g.lc (3% OV1 on chromosorb w). The F.I.D. response factors were assumed to be the same for each product. In each experiment product ratios were constant or changed only slowly with longer reaction times and total yields of products were always comparable. The glc peaks were identified by mass spectrometry and by comparison with the pure compounds prepared by reaction of the quinone methide with each solvent alone.

From the results, which are given in Table I, the order of ease of addition in neutral solutions is EtOH > *iso*PrOH > H_2O. In the presence of acetic acid the order is EtOH > *iso*PrOH > H_2O > HOAc.

TABLE I: Reaction of Quinone Methide (I) with Hydroxylic Solvents

Solvents - Equimolar mixtures of:				Ratio of Products, Phenol (II)			
H_2O	EtOH	*iso*PrOH	HOAc	R= OH	OEt	*iso*PrO	OAc
x	x			1	3.1	-	-
x		x		1	-	1.1	-
x	x	x		1	3.3	1.3	-
x			x*	1	-	-	0.8
x	x		x	1	10	-	-
x		x	x	1	-	1.7	-
x	x	x	x	1	3.9	1.7	-

* t-BuOH was added to give one phase; no t-BuOH addition product was detected.

Competitive Addition of Hydroxylic Solvents and their Conjugate Bases

In two similar series of experiments the quinone methide was added

a) in benzene to mixtures of ethanol (23g) and a range of acetic acid - sodium acetate buffers in water (10g) and

b) in pentane to mixtures of N_1N_1 - dimethylformamide (DMF) (10 ml) and a range of acetic acid-sodium acetate buffers in water (10g).

In the latter experiments the pentane was evaporated rapidly to leave a homogeneous aqueous DMF phase.

The results, which are given in Tables (II) and (III) respectively, show that the addition of water is not favoured if either ethanol or buffered sodium acetate is present. In what are probably weakly acidic (or neutral) solutions, acetate ions appear to be able to compete very effectively with ethanol or water for the addition to the quinone methide.

As the solution becomes more basic due to the hydrolysis of acetate, ethoxide and/or hydroxide ions would be formed. These ions are stronger nucleophiles than acetate [3], and the relative amounts of the products formed by their addition to the quinone methide increases significantly. In mixtures probably containing both ethoxide and hydroxide ions, ethoxide appears to add more readily. The order of ease of addition in these experiments appears to be $EtO^- > OH^- > OAc^- > EtOH > H_2O > HOAc$.

TABLE II: Reaction of Quinone Methide (I) in HOAc/NaOAc/H_2O/EtOH mixtures

Reactant Concentrations (Moles/l)				Ratio of Products, Phenol (II)		
HOAc	NaOAc	H_2O	EtOH	R= OH	OEt	OAc
0.4	0	10	10	0.2	1	0.02
0.37	0.03	10	10	0.2	1	1.1
0.33	0.07	10	10	0.15	1	2.5
0.25	0.15	10	10	0.1	1	3.6
0.16	0.24	10	10	0.1	1	7.0
0.08	0.32	10	10	0.1	1	7.8
0.04	0.36	10	10	0.1	1	8.2
0.01	0.39	10	10	0	1	4.5
0.004	0.396	10	10	0	1	2.5
0.001	0.399	10	10	0	1	0.7
0	0.4	10	10	0.1	1	0.01

TABLE III: Reaction of Quinone Methide (I) in HOAc/NaOAc/H_2O/DMF Mixtures

Reactant Concentrations (Moles/l).			Ratio of Products, Phenol (II)	
HOAc	NaOAc	H_2O	R= OH	OAc
1.0	0	28	1	0.03
0.82	0.18	28	1	9.5
0.63	0.37	28	1	18.2
0.40	0.60	28	1	18.1
0.21	0.79	28	1	12.8
0.07	0.28	28	1	7.2
0.02	0.08	28	1	1.9
0.002	0.008	28	1	0.6
0	1.0	28	1	0

Conclusions

The order of ease of addition of simple hydroxy compounds or their conjugate bases to quinone methide (I) is similar to the order observed for their nucleophilicity in SN2 reactions[3]. By analogy lignin quinone methides should form lignin-carbohydrate ether and ester links, even in the presence of water, by reaction with carbohydrates or with glucuronic acid residues. The ether links may form readily at higher carbohydrate concentrations and seem likely to involve primary rather than secondary alcoholic hydroxyl groups. The ester links may occur frequently since they should be formed even at quite low glucuronic acid concentrations, as long as some of the acids are present as salts.

REFERENCES

1. Y.Z. Lai and K.V. Sarkanen in "Lignins", ed. K.V. Sarkanen and C.H. Ludwig, Wiley-Interscience, New York, 1971, p.220.
2. H. Hemetsberger and D. Knittel, Monatsh., 102 1110(1971).
3. J. March, 'Advanced Organic Chemistry', McGraw-Hill, New York, 1968, pp.288-289.