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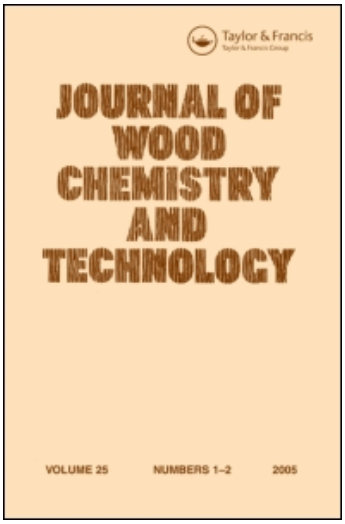

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The Mechanism of Cleavage of B-Ether Bonds in Lignin Model Compounds By Reducing Sugars

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THE MECHANISM OF CLEAVAGE OF β-ETHER BONDS IN LIGNIN MODEL COMPOUNDS BY REDUCING SUGARS

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ABSTRACT

The alkaline cleavage of β-ether bonds of phenolic lignin model compounds by reducing sugars has been shown to occur by the reaction of the quinone methide of the lignin model with a sugar-derived enediol. Reaction of the quinone methide of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethanol with L-ascorbic acid in the absence of base gives a carbon-carbon bonded intermediate formed by reaction of the C-2 carbon of the ascorbic acid enediol with the α-carbon of the quinone methide. This intermediate then fragments under alkaline conditions to guaiacol and vinylguaiacol, the same products as obtained from heating the β-ether itself with ascorbic acid or reducing sugars under alkaline conditions. The isolated intermediate was obtained as a one to one mixture of two stereoisomers, isomeric at the benzylic carbon, from which one isomer was selectively crystallised. The generality of the reaction and its relevance to the development of alternative pulping processes is discussed and the possibility of carbon-carbon bonded lignin carbohydrate complexes being formed via enediols is suggested.

INTRODUCTION

In conjunction with our studies on the development of catalysts for alkaline pulping it was recently found that compounds derived from reducing sugars are capable of cleaving β -ether bonds in phenolic lignin model compounds under alkaline

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conditions.[1,2] Such a finding is of both fundamental and practical significance as splitting of this bond in the lignin macromolecule is believed to be the critical reaction in the delignification process. To gain an understanding of the mechanism by which such reactions occur a study was initiated to synthesise likely intermediates and examine their reactions under alkaline conditions.

In our earlier studies[2] the effectiveness of various reducing sugars at cleaving the lignin model compound guaiacylglycol- β-guaiacyl ether was gauged by measuring the yields of guaiacol and vinylguaiacol obtained after reaction with the sugars in 1N sodium hydroxide at 135°C for one hour. This provided considerable evidence to suggest that the cleavage of the β-ether bond was occurring by base fragmentation of an intermediate formed by the reaction of a quinone methide of the β-ether with a sugar-derived enediol. That a quinone methide was involved was indicated from the lack of reactivity of the lignin model in which the phenolic group was methylated. The participation of an enediol in the reaction was supported by the ineffectiveness of non-reducing sugars and the fact that ascorbic acid was more effective than glucose or any of the other simple reducing sugars examined.

Based on this information the reaction pathway shown in Scheme 1 involving formation of a carbon-carbon bonded intermediate was formulated as being the most reasonable. This intermediate may then be expected to undergo a Grob fragmentation under basic conditions to give the observed products, guaiacol and vinylguaiacol, plus a presumably unstable diketo sugar. Such a fragmentation scheme is entirely analogous to that proposed for the β-arylether-anthrahydroquinone adduct previously isolated.[3]

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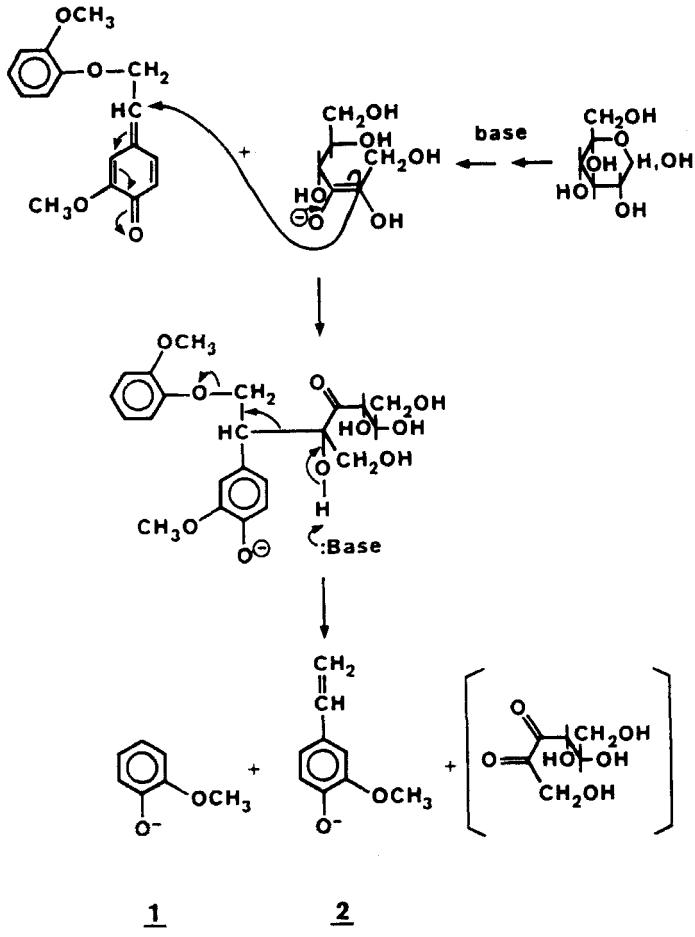
SCHEME 1



1 2

Enediols of the type shown in Scheme 1 are formed during the base catalysed isomerisation of glucose by a pathway known as the Lobry de Bruyn van Ekenstein transformation[4] in which the glucopyranose ring first opens to the acyclic aldehyde which then tautomerises to the enediol and reketonises to give either glucose, mannose or fructose. Other enediols are also formed during base catalysed degradation of C-6 sugars including C-3 fragments formed via reverse aldol reactions of the ketose and

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1,2-enediol forms of the sugars.[5] Because of the large number of possible intermediates that could be formed from the reaction of glucose with the β-arylether, ascorbic acid was chosen as the enediol for the mechanistic study. In contrast to the glucose- derived enediols this compound was readily available and relatively stable. It was also known from the earlier study[2] to give a high proportion of β-ether cleavage products. The expected intermediate from the reaction of ascorbic acid with the β-arylether quinone methide and its expected fragmentation is shown in Scheme 2. This is entirely analogous to that proposed in Scheme 1 except for the additional hemiketal cyclisation step which ascorbic acid derivatives are known to undergo.

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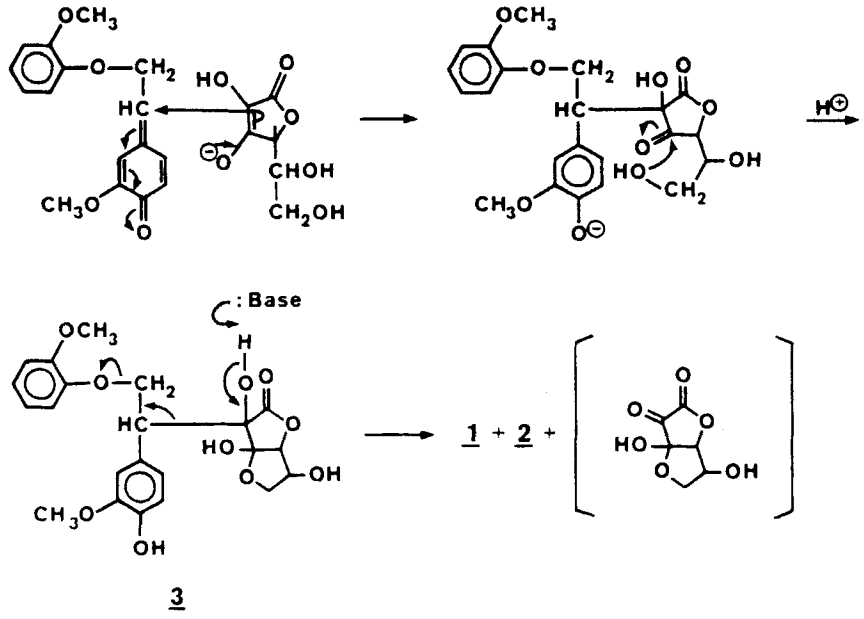
RESULTS AND DISCUSSION

Synthetic Method

Initial attempts to synthesise the proposed intermediate 3 by the reaction of the quinone methide with ascorbic acid under alkaline conditions were unsuccessful, giving only unreacted starting material or polyphenolic compounds depending on the severity of the conditions. However, during this study a report was published on the reaction of L-ascorbic acid with α,β-unsaturated compounds under neutral conditions to give carbon- carbon bonded products of the type of interest to us.[6] This prompted us to repeat our reaction under neutral conditions which resulted in the successful isolation of what appeared to be a β-arylether-ascorbic acid adduct. The quinone methide for the reaction was generated by the reaction of the β-arylether with bromotrimethylsilane and subsequent treatment of the intermediate bromide with sodium bicarbonate solution.[7] The resultant solution of the quinone methide in dichloromethane,

SCHEME 2



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free of aqueous bicarbonate, was then added to an aqueous solution of ascorbic acid. Presumably because of the two phase nature of the reaction the yield of product was relatively low. However, this was improved substantially by adding acetonitrile to the aqueous solution of ascorbic acid to give a 29% yield of product and 27.8% recovered starting material.

Structure Proof

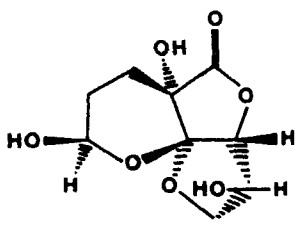
The product was purified by prep. t.l.c. and its molecular weight confirmed as 448 by chemical ionisation-mass spectrometry. The C-13 n.m.r. spectrum indicated that the product was a one to one mixture of two stereo isomers of compound 3. Crystallisation of this material from chloroform gave a colourless crystalline solid which was predominantly one isomer by C-13 n.m.r. The

formation of only two stereoisomers out of a possible eight from the three new asymmetric centres generated in the formation of the product is consistent with previous studies of other ascorbic acid condensation products. In particular, compounds 4[6] and 5[8] (shown below) were both obtained as just one isomer. Their structures were determined by X-ray crystallography.

Apparently formation of the carbon-carbon bond at C-2 occurs from the side of the molecule opposite to the C-5, C-6 substituent on C-4. This is then followed by ring closure of C-3 with the oxygen on C-6 to form the hemiketal with the thermodynamically favoured cis ring junction of the two five membered rings. A similar sequence of events in the present case would result in structure 3b isomeric at the α carbon of the β-arylether unit giving two stereoisomers.

Fragmentation Reaction

Following the successful synthesis of the proposed intermediate in the reaction of ascorbic acid with the β-arylether the validity of the proposed mechanism was then determined by the reaction of this intermediate under the conditions previously used for the β-ether cleavage studies. This was expected to fragment to guaiacol, vinylguaiacol and the diketo sugar as shown in Scheme 2.



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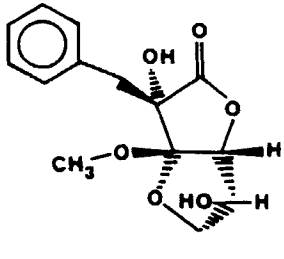

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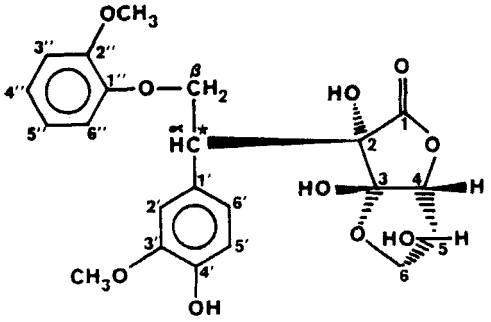

3b

Reaction of the crystalline product and the one to one isomeric mixture of compound 3 at 135°C for one hour in 1N NaOH both gave the predicted products guaiacol and vinylguaiacol. The yield of guaiacol from both was 52%. This compares with 66% from the reaction of the β-ether with ten equivalents of ascorbic acid and 30% with one equivalent of ascorbic acid. In these cases other enediols formed by degradation of ascorbic acid under the basic conditions will also be involved in the fragmentation of the β-ether. However, the low yield of guaiacol when one equivalent of ascorbic acid is used indicates that this is much less efficient than fragmentation of the isolated intermediate. The diketo sugar is presumably unstable and was not isolated from the reaction mixture.

CONCLUDING REMARKS

β-Ether Cleavage by Reducing Sugars

The isolation of the β-arylether-ascorbic acid adduct and its subsequent fragmentation to guaiacol and vinylguaiacol with cleavage of the β-ether bond indicate that this is the

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mechanism by which enediols derived from reducing sugars promote the cleavage of lignin model compounds. Although enediols of this type would not be expected to be very stable under alkaline pulping conditions they are generated continuously during alkaline pulping and may maintain a steady state concentration and thus could play a part in the delignification process. Participation of reducing sugars or their degradation products is already the basis for the mechanism of anthraquinone (AQ) pulping as without a reducing source the active anthrahydroquinone component would not be generated. The participation of sugars or their degradation products in the pulping process in this way has previously been totally overlooked.

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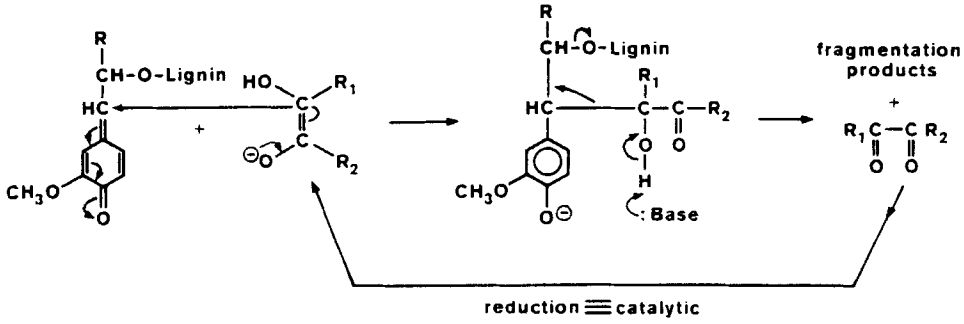
The Development of Alternative Pulping Agents

As well as providing an explanation as to how reducing sugars cleave the β-ether bonds of lignin model compounds the results of this study may also be relevant to the development of alternative alkaline pulping processes by providing an insight into what functional groups are required for a molecule to promote degradation of the lignin polymer.

Based on the results of this study it is reasonable to assume that any enediol which is stable under alkaline conditions will promote cleavage of phenolic β-ether bonds by fragmentation of a carbon-carbon bonded intermediate as shown in Scheme 3. This is supported by our current studies, to be reported separately, which have demonstrated the ability of a range of enediols to cleave the β-ether bond.

If the diketo product is reduced back to the enediol the system then becomes catalytic and this is exactly what occurs with AQ in which AHQ may be considered to be an alkali stable vinylogous enediol. It is interesting to note that the

SCHEME 3



potential use of enediols as pulping catalysts was suggested as early as 1978.[9] However, few studies have been done on this class of compounds since then.

Lignin-Carbohydrate Bonds

The isolation of an alkali sensitive lignin-carbohydrate type compound also raises the possibility that carbon-carbon bonded lignin carbohydrate complexes (LCC's) may be formed during the lignification process. For this to occur all that is required is that quinone methides be generated in the lignin precursors and it is known that such functionalities can be generated during dehydrogenative polymerisation of lignin.[10] Until now it has been generally believed that all LCC's are linked by either ether[11,12] or ester[13] bonds. However, because of the sensitivity of carbon-carbon linked LCC's to alkaline hydrolysis it is quite possible that they have previously been overlooked.

In two previous studies on the nature of LCC bonds in which phenylpropane lignin model compounds have been reacted with simple sugars the only LCC type product isolated has been the

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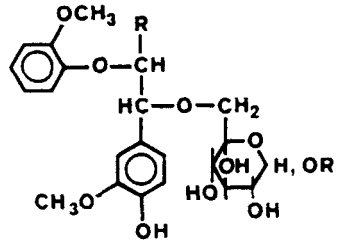

6

ether in which the α carbon of the lignin model is linked to the C-6 oxygen of the sugar as shown in compound 6.

In each of these studies the conditions were such that the isolation of any carbon-carbon bonded products would not have been expected. In the first study[10] the quinone methide was reacted with the sugar under neutral conditions and thus none of the enediol isomerisation products necessary for carbon-carbon bond formation would have been generated. In the second study[14] alkali was present during the reaction which would have resulted in fragmentation of any carbon-carbon bonded LCC's as they were formed.

In summary it is our belief that the isolation of a carbon-carbon bonded intermediate of the type described in this paper may provide an important contribution to increasing our understanding of the role played by reducing sugars in the pulping process, the development of new pulping catalysts and the nature of lignin-carbohydrate bonds.

EXPERIMENTAL

Synthesis of Intermediate 3b

The required quinone methide was generated by reaction of 1-(4-hydroxy-3-methoxyphenyl)-hydroxy-2-(2-methoxyphenoxy)

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ethanol[15] (0.4 g) with bromotrimethylsilane (450 µl, 2.5 eq) in dichloromethane (60 ml) for 2 minutes at 20°C followed by reaction of the resultant bromide with saturated aqueous sodium bicarbonate solution.[7] The resultant yellow solution of the quinone methide in dichloromethane was then separated, dried over magnesium sulphate, filtered and added to a rapidly stirred solution of L-ascorbic acid (1.23 g) in acetonitrile (40 ml)-water (5 ml) under nitrogen. After stirring the mixture for 3 hours at 20°C the acetonitrile was removed under reduced pressure and water (15 ml) added. The product was then extracted with dichloromethane (2 x 50 ml) and re-extracted with ethyl acetate (2 x 50 ml) after addition of sodium chloride. Both extracts were dried over magnesium sulphate, filtered and concentrated to dryness. The dichloromethane extract (345.5 mg) was purified by prep. t.l.c. ($CHCl_3$:EtOAc:HOAc 4:4:1) to give recovered β-arylether starting material (R_f 0.6, 111.3 mg, 27.8%) and compound 3b (R_f 0.3, 161.3 mg, 26.1%). Purification of the ethylacetate extract (80.3 mg) in the same way gave a further 18 mg (2.9%) of product 3b.

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The ^{13}C n.m.r. spectrum of purified 3b indicated that it was a 1:1 mixture of two stereochemical isomers of the desired product. MS (CI CH_4 0.6 Torr), m/z (relative intensity) 475(1.4), 448(M^+) (1.5), 447(1.7), 315(1.1), 301(2.2), 287(1.9), 273(22.6), 195(5.1), 165(16.8), 151(32.7), 137(22.3), 125(100). Crystallisation of the mixture from chloroform gave a single isomer (isomer A) as colourless needles (m.p. 104-105°).

Isomer A ^{13}C n.m.r. (22.5 MHz) δ (d_6-acetone) 51.63(αC), 56.25(aromatic OMe's), 69.32(βC), 75.05(C6), 75.24(C4), 82.20(C2), 87.14(C5), 108.86(C3), 113.67, 114.97, 115.10, 115.36(C2', C3", C5', C6") 121.80, 122.13(C5", C6'), 124.14(C4"), 127.78(C1'), 147.03, 147.68, 149.63(C2", C3', C4'), 150.67(C1"), 176.03(C1).

Isomer B ^{13}C n.m.r. (22.5 MHz) δ (d_6-acetone) (determined in admixture with isomer A) 48.90 (α C), 56.32(aromatic OMe's) 70.36(β C), 75.38(C6), 75.16(C4), 81.53(C2), 86.71(C5), 108.43(C3), 114.06, 114.79, 115.33, 115.54(C2', C3", C5', C6"),. 121.89, 122.29(C5", C6'), 123.62(C4"), 128.26(C1'), 146.95, 147.74, 149.71(C2", C3', C4') 150.88(C1"), 175.47(C1).

Fragmentation Reaction

The isomeric mixture of adduct 3b (29.4 mg) was dissolved in 1N NaOH (5 ml) under nitrogen and heated in a sealed tube at 135°C for 1 hour. Analysis of the chloroform extract as described previously[2] gave a 52.0% yield of guaiacol and 5.1% yield of vinylguaiacol. The same reaction at 60°C for 1 hour gave 37.2% guaiacol and 1.6% vinylguaiacol. Reaction of the crystalline isomer A under the same conditions gave a 52.2% guaiacol and 3.7% vinylguaiacol.

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