Studies on the Condensation of Lignins in Alkaline Media. Part III.*
The Formation of Stilbenes, Arylcoumarans and Diarylmethanes on Treatment of Spruce Wood Meal with Alkali and White Liquor in the Presence of Xylenols

JOSEF GIERER and OTTO LINDEBERG

Swedish Forest Products Research Laboratory, Chemistry Department, Box 5604, S-114 86 Stockholm, Sweden

Recently, it has been shown that model compounds representing phenolic lignin structures of the β-aryl ether type (A, R = H) react with simple phenols in alkaline solution to give primary condensation products. These may subsequently undergo neighbouring group participation reactions with cleavage of the β-aryl ether linkage, as shown in Scheme 1 (upper part) and described in Ref. 1. Formaldehyde, liberated from terminal hydroxymethyl groups in quinone methide intermediates, 1,2 reacts with the added phenol affording the corresponding diarylmethane 1 (see lower part of Scheme 1).

The aim of the present work is to confirm the validity of the results from these model experiments.

Experimental. Spruce wood meal (1.5 g), pre-extracted with acetone, was treated with sodium hydroxide (2.2 M), and sodium hydroxide (2.1 M) containing sodium sulfide (0.2 M) ("white liquor") * (15 ml of each), at 170 °C for 1.5 and 4 h in the presence of 2,4- or 2,6-xylenol (0.2 M). The resulting cooking liquors were filtered, an aliquot was neutralized (10 % H₃PO₄) and, after addition of an internal standard (piperonal), extracted with chloroform. The extract was centrifuged, dried (Na₂SO₄) and evaporated, and the residue was acetylated (acetic anhydride—pyridine). Identification of the acetates was performed by HPLC and GC-MS (comparison of retention times and mass spectra with those of authentic samples) with the exception of the diacetate of 3 which was identified only by GC-MS. Quantitative estimates of 3, 5 and 7 were made on the basis of HPLC data.

The results from the treatments are summarized in Table 1. As can be seen, arylcoumaran 3, stilbene 5 and diarylmethanes 6 and 7 were all found in the corresponding liquors.

The presence of 3 and 5 in the cooking liquors is consistent with the behaviour of phenolic lignin units of the β-aryl ether type (A, R = H) expected on the basis of the results from model studies. 1,4 The formation of 3 rather than 3α indicates that elimination of formaldehyde from quinone methide intermediates of type B (R = H) 4 proceeds faster than the conjugate addition of the carbanion from 2,4-xylenol. In other words, the carbanion from 2,4-xylenol adds to β-aroyxy styrene structures (C), arising from quinone methide intermediates of type B by formaldehyde elimination, rather than to B. 4

This was supported by reacting cis-4-hydroxy-3-methoxy-β-guaiacyloxy-styrene with 2,4-xylenol in alkaline solution and demonstrating the presence of 3 (2.3 %) in the reaction mixture. The formation of 3 instead of 3α was confirmed by treating 1 (R = CH₂OH) with 2,4-xylenol in alkali and in white liquor for 4 h, and isolating 3 in yields of 3.0 and 0.6 %, respectively. Compound 3α was not found in the reaction mixtures.

In view of the abundance of phenolic β-aryl ether structures (A), originally present in lignin and liberated during the alkaline treatment, the term "white liquor" refers to a solution of NaOH (8.4 g) and Na₂S.9H₂O (4.8 g) in distilled water (100 ml).

* The term "white liquor" refers to a solution of NaOH (8.4 g) and Na₂S.9H₂O (4.8 g) in distilled water (100 ml).

** The reverse holds true for the more reactive carbanion from resorcinol, as has been shown in model experiments.

0302-4369/79/080580-03$0.25 © 1979 Acta Chemica Scandinavica
The amounts of 3 and 5 found seem to be surprisingly low. However, there are several requirements to be met if these structures are to give 3 or 5 as low molecular degradation products:

1. The structure must contain a free phenolic hydroxyl group and an α-substituent which can be eliminated to give a quinone methide intermediate (B) in the rate determining reaction step.7

2. The added phenol has to compete successfully with other nucleophiles, present in the cooking liquor, for the quinone methide intermediate.7

3. The phenolic β-aryl ether structure (A) must not be linked in the ortho-position to an adjacent arylpropene unit, i.e. R in A has to be H ("uncondensed" unit). "Condensed" units (R = adjacent arylpropene unit) can be expected to undergo analogous transformations.7

However, the resulting arylcoumaran and stilbene moieties will remain attached to the residual lignin or lignin fractions.

Anticipating that all β-aryl ether bonds in phenolic units are cleaved via the mechanisms outlined in Scheme 1 (upper part) and those in non-phenolic units via the oxirane mechanism, and assuming that about half of all β-aryl ether units (totally 48 β-aryl ether bonds per 100 arylpropane units) are of the "uncondensed" type and only 20% of these are able to form quinone methide intermediates, the maximum yields of 3 and 5 would be $48 \times 0.5 \times 0.20 = 4.8\%$. The discrepancy between these calculated yields and those actually obtained may be ascribed to incomplete reactions of the β-aryl ether structures (cf. behaviour of model compounds), to secondary reactions of 3 and 5 during the treatments, e.g., condensation reactions, and to losses during the work-up procedure.

As shown in Table 1, the yields of 5 are 2–6 times higher than those of 3 indicating that the carbocation from 2,6-xylenol is more reactive than that from 2,4-xylenol. This is also reflected by the yields of 3 and 5 obtained after treatment in alkali compared with those obtained after treatment with white liquor. The yields of 3 are reduced to one half by the presence of hydrosulfide ions in the cooking liquor, whereas the yields of 5 during the first 1.5 h remain unaffected. Thus, under the conditions used, hydrosulfide ions compete with carbocations from 2,4-xylenol for the β-aroxyl styrene intermediates (C) to an appreciable degree, whereas they compete much less effectively with carbocations from 2,6-xylenol for the quinone methide intermediates B (cf., however, Ref. 7).

The formation of diarylmethanes 6 and 7 shows that a small proportion of the formaldehyde expected to be liberated from intermediary quinone methide structures is trapped and thus prevented from condensing with phenolic lignin units. In a separate experiment, the same amount of formaldehyde as expected from a quantitative elimination of all hydroxy methyl groups was treated with an excess of 2,6-xylene in 2.2 M alkali or white liquor. Compound 7 was isolated after both treatments in a yield of only 8% indicating that the major part of the formaldehyde is consumed by autocondensation.

In addition to the compounds given in Table 1, the reaction mixtures contained minor amounts of further xylenol derivatives and monomeric and oligomeric products, also obtained on similar treatments of wood meal without addition of xylenols (as shown by GC-MS).

The total extent of β-aryl ether cleavage and the structural changes in residual lignins resulting from the presence of xylenols in the alkaline cooking liquors are currently being studied.