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Dibenzodioxocins; A Novel Type Of Linkage In Softwood Lignins

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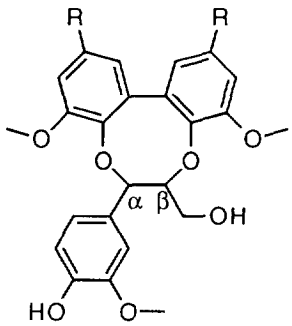
Abstract Correlation peaks found in HMQC spectra of softwood lignins have been assigned to a dibenzodioxocin structure with the aid of model compounds. It constitutes a major hitherto unknown structure in softwood lignins.

In our recent work on the elucidation of the structure of lignins using 2-D NMR techniques[1] we have drawn attention to some correlation peaks that we have been unable to assign to any known type of linkage in lignins. For instance, when running ^{1}H-detected multiple quantum ^{1}H-^{13}C correlation (HMQC)[2] spectra on softwood MWL preparations, we found prominent correlation peaks at 4.84/84.20 and 4.15/82.51 ppm.[1] A homonuclear Hartman-Hahn (HOHAHA)[1] experiment revealed that the carbon atoms were adjacent in the same structural unit. We could not assign them to any currently proposed side chain structure in lignins and we attributed them to some new type of inter-unit linkage. We now wish to report that we can assign these correlations to a new linkage that is biosynthetically plausible and that is in accord with currently known analytical data on softwood lignins.

Model compounds with a dibenzodioxocin structure (**1**) give correlations that exactly coincide with the unknown correlations in softwood lignin spectra (Figures 1 and 2).



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We have demonstrated with model experiments that structure (**1**) can be formed during biosynthesis by oxidative coupling of a lignin precursor with a 5-5 iphenyl structure in the growing lignin polymer.

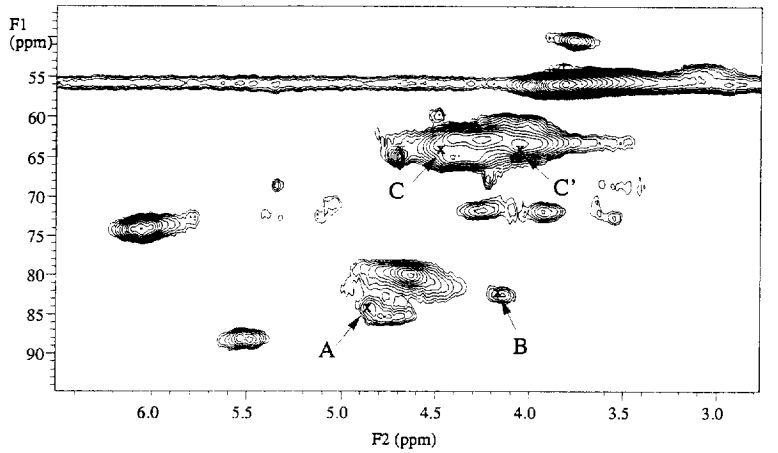

Figure 1. Expansion of the 2D HMQC spectrum of acetylated pine milled wood lignin (MWL). Correlations A and B can not be assigned to any of the currently proposed side-chain structures in lignins. The x's indicate superimposed correlation positions of an acetylated model compound of structure 1. The correlations are: Hα/Cα in 1 4.86/84.01 and A 4.84/84.20; Hβ/Cβ in 1 4.16/82.37 and B 4.15/82.51; Hγ/Cγ in 1 are at 4.51/63.48 and 4.05/63.48, C and C' in MWL are obscured by correlations from other structural units.[1]

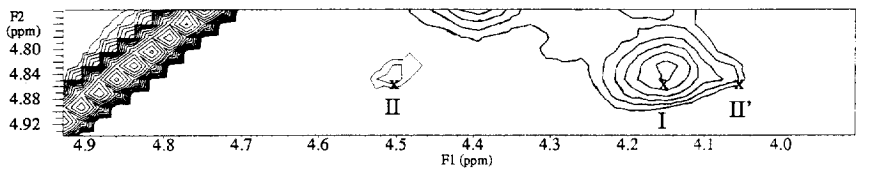

Figure 2. Comparison of expected HOHAHA correlations (marked with x) of an acetylated model compound of structure 1 with an observed 2D HOHAHA spectrum (mixing time = 120 ms) of acetylated pine MWL. The correlations are: Hα/Hβ (expected 4.86/4.16, observed (I) 4.84/4.15) and Hα/Hγ Hγ' (expected 4.86/4.51 and 4.86/4.05 observed (II) 4.84/4.50 and (II') 4.84/4.07).

Molecular models of this 8-membered ring system do not exhibit any conformational or other strain.[3] In spite if its apparent stability we have not been able find any previous mention of a natural product containing this structure. The syntheses of the model compounds for this structure will be published separately. The new structural element involves the biphenyl structures in lignins. The proportion of biphenyls is rather large in softwood lignins: according to current estimates[4-6] 19 to 26% of phenylpropane units are involved in such units. The discovery of a new 8-membered ring system involving the biphenyl goups in softwood lignins thus has important consequences for the study of lignin reactivity both in biodegradation and in pulping of wood.

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