# Phenylcoumaran Elements in Spruce Lignin

ERICH ADLER, SUNE DELIN and
KNUT LUNDQUIST

*Institutionen för organisk kemi, Chalmers
Tekniska Högskola, Göteborg, Sweden*

Dihydro-dehydrodiconiferyl alcohol (I)[1] and its monomethyl ether (II)[1], on heating with 0.2 N HCl in methanol or in dioxane-water (9:1), are converted into the phenylcoumarone derivatives III and IV, respectively[2]. This conversion of a hydroxymethyl-substituted phenylcoumaran into a methyl-substituted phenylcoumarone can readily be accounted for by a sequence of ring opening, allylic rearrangement and recyclisation[2].


I : R= H   III : R=H
II : R= CH₃   IV : R =CH₃
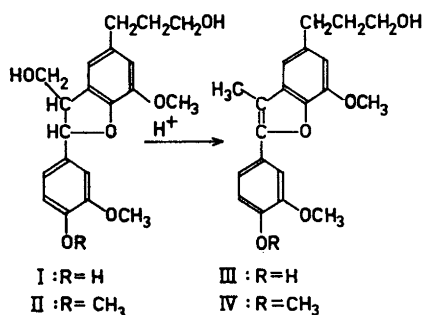
The absorption spectrum of the phenolic coumarone derivative (III), m.p. 172–173° (diacetate, m.p. 114°), shows a maximum at 310 mμ (ε, 27 000) in ethanolic solution and a maximum at 326 mμ (ε, 31 400) in alkaline ethanolic solution. These spectra and the "ionisation $\Delta\varepsilon$" curve (λ_{max} 338 mμ, ε, 27 000) obtained from them are very similar to those previously reported[3] for a related coumarone[4] obtained by dehydrogenation of dihydro-dehydrodiisoeugenol with sulphur. The absorption spectrum of the non-phenolic coumarone IV in ethanol is similar to that of III in the same solvent. Spectrophotometric examination of the reactions I → III and II → IV revealed that a maximum conversion of about 70 % was obtained after 20 h in a boiling 0.2 N HCl dioxane-water mixture.

Dehydrodiconiferyl alcohol (V) is formed, together with other products, by enzymatic dehydrogenation of coniferyl alcohol[1], and the phenylcoumaran system (VIa and VIb, with various modifications of the side-chain of the phenylpropane moiety A) is assumed[5] to be present in lignin.

In the present investigation an attempt has been made to demonstrate, by spectrophotometric analysis, the formation of phenylcoumarone systems (type VII) from phenylcoumaran elements (type VI) on treatment of spruce Björkman lignin with hot acid and to estimate the frequency of phenylcoumaran elements in the lignin. A solution of Björkman lignin in dioxane-water (9:1) containing 0.2 N HCl was refluxed for 21 h. As shown in previous work[6], such treatment of lignin ("acidolysis") converts arylglycerol-β-aryl ether elements into arylpropanone structures of various types ("Hibbert ketone" structures), including arylpropanone-1 and arylpropanedione-1,2 structures. These being

V

VIa : R=H
VIb : R=C of propane side-chain of adjacent monomer

VIIa : R=H
VIIb : R=R in VIb
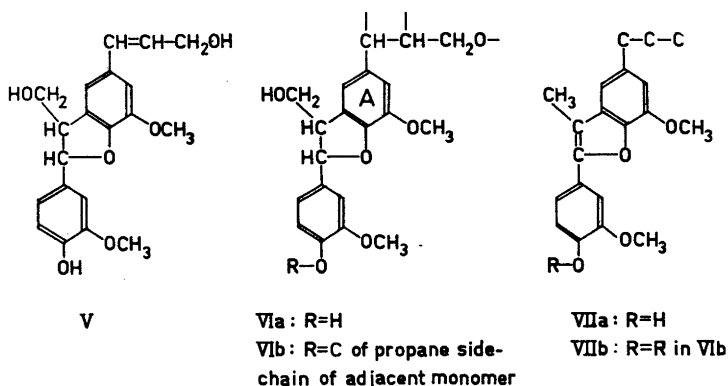
aryl α-ketones have strong light-absorption in the region of 310 mμ and thus would interfere with the intended spectrophotometric determination of the arylcoumarone systems (VII). The acid-treated lignin solution was therefore made alkaline and treated with sodium borohydride to eliminate any carbonyl groups present [7]. From the absorption curve of the reacidified solution a Δε curve was obtained by "subtraction" of the absorption curve of a similar lignin solution which had been reduced with borohydride and then reacidified but which had not been subjected to "acidolysis". This Δε curve showed a distinct band with a maximum at 310 mμ and a shape very similar to that of the main absorption band of the arylcoumarones III and IV. This indicates that arylcoumarone systems (VIIa + VIIb) were actually formed during the hot acid treatment of the lignin and, consequently, that arylcoumaran elements (VI) were present in the original lignin. Comparison of the Δε value at 310 mμ with the corresponding value for the model conversion I→ III indicated that in the Björkman lignin sample used, about 18 % of the phenylpropane units were present in dimeric elements of the phenylcoumaran type (VIa + VIb).

To investigate the proportion of phenolic coumarone elements (VIIa) formed, "ionisation Δε" curves were obtained for the carbonyl-free acidolysis lignin, and for carbonyl-free lignin which had not been subjected to acidolysis. From these two curves a difference curve was prepared which was expected to be the "ionisation Δε" curve for the phenolic guaiacylcoumarone systems (VIIa) formed in the acidolysis. The position of the main band of this difference curve (max 338 mμ) was in fact identical with that of the corresponding band obtained in a model experiment (I → III). Comparison of the Δε values at 338 mμ for both experiments indicated that about 16 % of the phenylpropane units in the Björkman lignin used had given a phenolic coumarone system (VIIa). The fact that the major part of the coumarone was of the phenolic type (VIIa) rather than the ether type (VIIb) is explained by the previous finding [6] that acidolysis of lignin liberated a considerable amount of phenolic hydroxyl groups.

Preceding work [6] has shown that about 25 % of the phenylpropane units in spruce Björkman lignin are of the phenylglycerol type linked by a β-aryl ether bridge to the adjacent monomer, or in other words, that

up to 50 % of the lignin may consist of dimeric elements of the guaiacylglycerol-β-dihydroconiferyl ether type. The present study indicates that nearly 20 % of the lignin is made up of phenylcoumaran dimers (VIa + VIb). Although the various dimeric elements may "overlap" to some extent, one or both of the two phenylpropane moieties of a dimeric element also forming part of a following one, the results obtained account for the structural elements of an appreciable part of the total average lignin molecule.

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Determination of ε-Aminocaproic Acid in Urine by Means of High-Voltage Paper Electrophoresis

ALBERT SJOERDSMA* and ARNE HANSON

Medical Clinic and Department of Clinical Chemistry, General Hospital, Malmö, Sweden

It has been reported that ε-amino-n-caproic acid (ε-ACA) is a potent inhibitor of plasminogen activation in vitro [1,2]. Preliminary studies in this hospital by Nilsson et al.[3] suggest that the compound may also be effective in vivo in the treatment of fibrinolysis associated with various diseases. It was therefore desirable to obtain information about the fate of ε-ACA in the body and to determine whether it is absorbed efficiently from the intestinal tract. To accomplish this a method for the estimation of ε-ACA in urine was needed.

* Visiting scientist, National Heart Institute, Bethesda 14, Maryland, U.S.A.