

Carbonyl Groups in Lignin

III. Mild Catalytic Hydrogenation of Björkman Lignin

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Björkman lignin was subjected to catalytic hydrogenation at room temperature in 93 % acetic acid in the presence of a Pd-BaSO₄ catalyst promoted by HCl (system A) or in alkaline solution with a nickel boride catalyst promoted by chromium boride (system B). The hydrogen consumption amounted to 0.5–0.6 moles of H₂/OCH₃ in system A, and to nearly 0.3 moles of H₂/OCH₃ in system B. Hydrogenation of the aromatic nuclei was negligible in both systems.

In system A only a minor fraction of the benzyl alcohol and benzyl ether groups suffered hydrogenolysis. The resistant main part of these groupings may belong to elements of the arylglycerol-β-aryl ether structure (V), which in model experiments was found to be hydrogenolysed very slowly. In system B the benzyl alcohol and benzyl ether groupings remained entirely intact.

In accordance with previous results, Björkman lignin was found to contain 0.03–0.04 cinnamaldehyde units per OCH₃. In addition, 0.03 ethylene groups were found, presumably present in cinnamyl alcohol units. These conclusions were reached by spectrochemical examination of the hydrogenated lignin products. Hydrogenation in system B indicated a total carbonyl content of about 0.2 CO/OCH₃, which is in harmony with the value previously found by oximation.

In Part II¹, experiments regarding the catalytic hydrogenation, at room temperature, of a great variety of lignin model compounds was reported. In the majority of the experiments 93 % acetic acid was used as a solvent, and the catalyst was prepared by hydrogenating PdCl₂-BaSO₄ immediately before the addition of the substance to be examined. The reaction mixture then contained a small amount of hydrochloric acid produced in the prehydrogenation of the catalyst. Some experiments were carried out in alkaline solution, with a nickel boride catalyst activated with chromium boride.

The results obtained with the palladium catalyst may be summarised as follows.

a) The benzyl-oxygen linkage of guaiacyl and veratryl ethyl carbinols (I) and their methyl ethers (II) was rapidly cleaved by hydrogenolysis, oxygen-containing substituents in the β and γ positions decreasing the rate of the reaction. The benzyl ether ring

was easily opened by hydrogenolysis in the two dimeric structures III (pinoresinol) and IV (phenylcoumaran type) and their ethers.

b) Hydrogenolysis of the benzyl-oxygen linkage was very slow in models representing the important lignin dimer structure V. Evidently, the β -aroxyl substituent and the γ -carbinol group decrease the reactivity of the benzyl grouping.

c) Ethylenic bonds either conjugated with the aromatic ring (as in coniferyl alcohol, VI) or isolated (as in eugenol) were rapidly hydrogenated under the conditions used.

d) Keto groups conjugated with the aromatic ring (α -carbonyl groups) were reduced at satisfactory rates in guaiacyl as well as in veratryl compounds (VIII). In coniferyl aldehyde (VII) both the carbonyl and the ethylenic groups were rapidly hydrogenated.

e) Isolated keto groups (β -carbonyl groups, IX) reacted extremely slowly.

It could not be expected, of course, that the potentially reducible elements present in lignin would react with hydrogen at the same rates as the corresponding structures examined in the model compounds. In the polymeric lignin

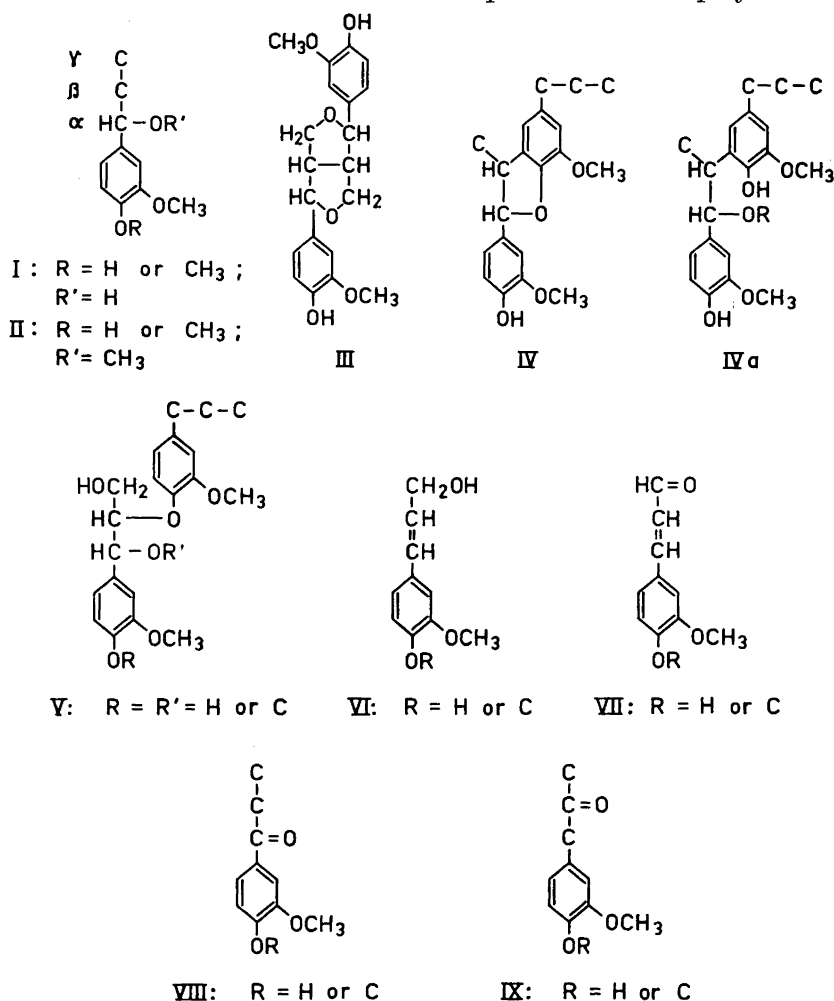


Table 1. Catalytic hydrogenation of lignin preparations (room temperature).

Expt.	Lignin preparation	Reaction mixture	H ₂ -pressure; time	Hydrogen consumption, moles of H ₂ per OCH ₃
1	Björkman lignin (Bj.L.)	0.1 g lignin, 0.5 g PdCl ₂ -BaSO ₄ , 15 ml 93 % HOAc	atm. press.; 24 h	0.5—0.6
2	Bj.L., reduced with NaBH ₄	as in expt. 1	atm. press.; 24 h	0.3—0.4
3	Bj.L.	as in 1, plus 0.05 g NaOAc	atm. press.; 24 h	0.2—0.3
4	Bj.L., methylated with CH ₃ OH-HCl	as in 3	atm. press.; 24 h	0.4—0.5
5	Bj.L.	1.2 g lignin, 8 g PdCl ₂ -BaSO ₄ , 100 ml 93 % HOAc	4 atm.; 70 h	not determined
6	Bj.L., methylated with CH ₃ OH-HCl	as in expt. 5	4 atm.; 70 h	• •
7	Bj.L.	1.0 g lignin, 0.7 g Ni-Cr-boride, 0.5 g NaOH in 50 ml EtOH- H ₂ O (1:1)	atm. press.; 6 h	0.3

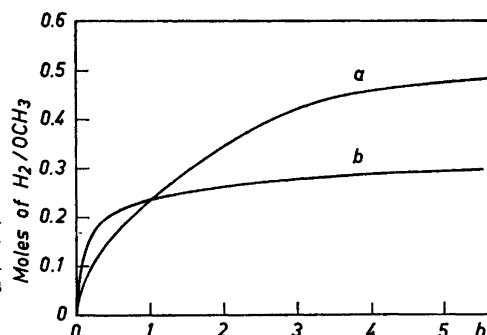
these elements are probably less accessible to the action of the catalyst and therefore will react more slowly. It was hoped, however, that the relative order of reactivity of the various structures in lignin would be similar to that observed in the low-molecular model compounds and that a study of the hydrogenation of lignin would provide information regarding the occurrence and the relative number of these structural elements.

A. HYDROGENATION OF BJÖRKMAN LIGNIN OVER PALLADIUM

When a solution of Björkman lignin in 93 % acetic acid was stirred in a hydrogen atmosphere over the prehydrogenated PdCl₂-BaSO₄ catalyst at atmospheric pressure, 0.4—0.5 moles of H₂/OCH₃ were consumed during a period of 4—5 h, values of 0.5—0.6 moles of H₂/OCH₃ being attained after about 24 h (Fig. 1, curve *a*, and Table 1, expt. 1). The hydrogen consumption was only 0.2—0.3 moles per OCH₃, if sodium acetate was added to the reaction mixture to eliminate the promoting action of the small amount of hydrogen chloride formed in the prehydrogenation of the PdCl₂ catalyst (Table 1, expt. 3). The hydrogenation of a Björkman lignin preparation, which had been pretreated with sodium borohydride² (see also Exptl.), resulted in the uptake of 0.3—0.4 moles of H₂/OCH₃ (Table 1, expt. 2). Experiments were also carried out at a hydrogen pressure of 4 atm. over a period of 70 h (Table 1, expt. 5).

The hydrogenated lignins recovered from the reaction mixtures in about 90 % yield were practically white. The IR absorption in the region of 1 700

Fig. 1. Hydrogenation of Björkman lignin with a Pd-catalyst (curve *a*, exptl. conditions see Table 1, expt. 1) and a nickel boride catalyst (curve *b*, exptl. conditions see Table 1, expt. 7).



—1665 cm^{-1} (aryl ketone and coniferyl aldehyde groupings) was considerably lower than in untreated Björkman lignin³.

Due to the presence of HOAc and HCl in the reaction mixture, partial acetylation of hydroxyl groups of the lignin took place, as indicated by analysis (the product obtained in expt. 1, Table 1, contained 0.68 $\text{CH}_3\text{CO/OCH}_3$) as well as by an absorption band at 1740 cm^{-1} . It is well-known, however, that acetylation of benzyl alcohol groups would not prevent the hydrogenolysis of such groups. This was also confirmed in the model experiments¹.

Fig. 2 gives the UV absorption curves of untreated Björkman lignin and of two of the hydrogenated products. The absorption values of the latter products at 280 $\text{m}\mu$ are only slightly lower than the corresponding value for Björkman lignin and are similar to that found for sodium borohydride-reduced lignin. This proves that no appreciable hydrogenation of the aromatic nuclei has taken place.

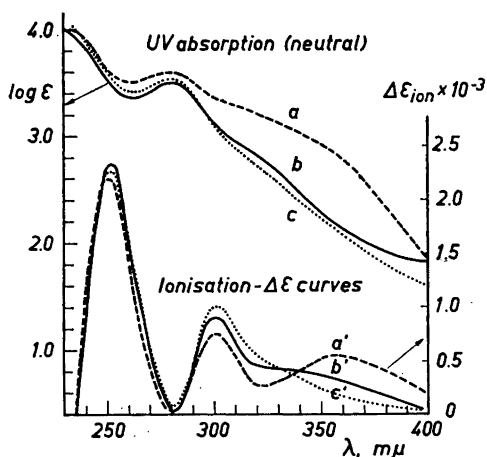


Fig. 2. UV-absorption in neutral solution and ionisation- $\Delta\epsilon$ curves. Solvents: Ethanol-ethylcellosolve (9:1) and 0.1 N NaOH in ethanol-ethylcellosolve-water (4:1:5), respectively. Curves *a* and *a'*: Untreated Björkman lignin. Curves *b* and *b'*: Hydrogenated Björkman lignin ($\text{PdCl}_2\text{-BaSO}_4$, 4 atm. H_2 ; see Table 1, expt. 5). Curves *c* and *c'*: NaBH_4 -reduced and subsequently hydrogenated Björkman lignin ($\text{PdCl}_2\text{-BaSO}_4$; see Table 1, expt. 2).

1. The benzyl alcohol and benzyl ether groupings in lignin.

According to the model experiments reported in Part II¹, it could be expected that the benzyl alcohol and benzyl ether groupings (structural types I, R and R' = H or C, III, IV, V) assumed to be present in untreated lignin or sodium borohydride reduced lignin, would undergo hydrogenolysis.

Hydrogenolysis of benzyl-oxygen linkages such as are present in structures of type I, R' = C, would involve a degradation of the lignin molecules. However, the solubility of the hydrogenated products did not differ significantly from that of original Björkman lignin, which tends to indicate that such hydrogenolysis did not occur to any great extent.

A closer examination of the behaviour of the benzyl alcohol and benzyl ether groups in the hydrogenation of Björkman lignin was made by studying the reaction of the hydrogenated products with cold methanolic hydrochloric acid. As demonstrated previously, Brauns lignin⁴ as well as Björkman lignin^{5,6} are methylated by this reagent, the latter lignin acquiring an average of 0.56 moles of OCH₃ per OCH₃ originally present. Since the borohydride-reduced lignins were methylated similarly, this introduction of OCH₃ could not be due to acetal formation, but was ascribed to the etherification and trans-etherification of benzyl alcohol and benzyl ether groups, respectively. Model experiments⁴⁻⁸ showed that both guaiacyl and veratryl carbinols and their non-cyclic ethers (types I, II and V) are etherified and trans-etherified, respectively, by CH₃OH-HCl at 20°. Under similar conditions, pinoresinol (III) yielded a resinous product with unchanged methoxyl content, and its dimethyl ether as well as the phenylcoumarans of type IV remained unaffected^{6,7}.

Reductive cleavage of the benzyl-oxygen linkages in lignin elements of types I, II, III, and V would cause such elements to become unreactive towards methanolic hydrochloric acid. It was found, however, that untreated as well as borohydride-reduced Björkman lignin, when subjected to catalytic hydrogenation (Table 1, expts. 1, 2, 5) and subsequently treated with cold methanolic hydrochloric acid, acquired 0.40—0.45 moles of OCH₃ per OCH₃ originally present. As there is no reason to doubt the correctness of the view that the presence of benzyl alcohol and benzyl ether groups in lignin is essentially responsible for this type of methylation, the result obtained indicates that the majority of these groups has resisted the hydrogenolytic attack. Only about 0.1 benzyl alcohol (benzyl ether) groups seem to have been removed.

Since hydrogen was consumed and, as will be shown below, ethylenic bonds and carbonyl groups were reduced, the fact that the majority of the benzyl-oxygen linkages survived, cannot be attributed to a general inefficiency of the hydrogenation system. It rather suggests that the benzyl-oxygen groups in lignin mainly belong to structural type V (arylglycerol- β -aryl ether type). In our model experiments (see Ref.¹, Table 1 and Fig. 1) these were found to be hydrogenolysed more slowly than the model types not carrying the β -aroxyl and γ -hydroxyl substituents. This would be in harmony with the view^{9,10} that type V constitutes a quantitatively important structural element in lignin.

A Björkman lignin preparation which had been treated with $\text{CH}_3\text{OH-HCl}$ (OCH_3 content, 22.33 %, corresponding to an uptake of 0.56 OCH_3 per OCH_3 originally present) was hydrogenated in the presence of sodium acetate (Table 1, expt. 4). Only 0.14–0.17 OCH_3 per OCH_3 originally present in the untreated lignin were removed. (In the absence of a buffering agent (expt. 6), 0.34 OCH_3 were eliminated, but in this case the HCl present may have caused some hydrolytic cleavage of the benzyl methyl ether groups.) Model experiments (see Ref.¹, Table 2 and Fig. 1) had shown that benzyl ether models of type V ($\text{R}' = \text{CH}_3$) carrying a β -aroxyl substituent undergo hydrogenolysis at a considerably lower rate than corresponding ethers lacking the β -aroxyl substituent. The slow and highly incomplete removal of OCH_3 on hydrogenation of methylated lignin seems to be in harmony with the suggestion that methylation had mainly taken place at aryl carbinol (ether) structures of type V.

As mentioned above, pinosresinol (III) and the phenylcoumarans (type IV) as well as the methyl ethers of III and IV are not methylated by methanolic hydrochloric acid at room temperature^{6,7}. Methylation of the hydrogenated lignin products would therefore give no information whether or not hydrogenolysis of these cyclic benzyl ether groupings has taken place. In the model experiments¹, compounds of type III and IV were more susceptible to hydrogenolysis than those of type V. Since the hydrogenolytic opening of the hydrofuran rings of pinosresinol¹¹ and of phenylcoumarans involves the liberation of one aliphatic OH/OCH_3 and of 0.5 phenolic OH/OCH_3 , respectively, similar reactions, if occurring in the catalytic hydrogenation of lignin, would be reflected in an increase of the number of hydroxyl groups.

The interpretation of such hydroxyl increase, however, is difficult. The hydrogenation of lignin will involve not only the hydrogenolytic liberation of aliphatic and phenolic OH , but also the formation of OH groups by the reduction of CO groups, and, furthermore, the disappearance of OH groups by reduction of aryl carbinol groupings. Estimation of the total number of acetylatable OH in hydrogenated lignins (from expts. 1 and 5, Table 1) indicated an increase of about 0.2 OH/OCH_3 as a result of the hydrogenation. Without going into details, this figure might be tentatively interpreted as involving, *inter alia*, the hydrogenolysis of pinosresinol elements amounting to about 10 % of the lignin molecule.

The liberation of phenolic hydroxyl which must take place on hydrogenolysis of the hydrofuran ring of phenylcoumarans seemed to provide a measure of the latter reaction. By the periodate method² as well as the ionisation- $\Delta\epsilon$ method¹², the number of phenolic OH in hydrogenated lignin (from expt. 5, Table 1) was found to be only 0.05 phenolic OH/OCH_3 higher than in untreated lignin. Assuming that the hydrogenolysis of the coumaran elements was complete, and that phenolic OH was liberated solely from such elements*, the figure obtained would indicate that 10 % of the lignin molecule

* Recently, K. Freudenberg and B. Lehmann [*Chem. Ber.* **93** (1960) 1354] briefly reported that the reaction mixture obtained on enzymatic dehydrogenation of coniferyl alcohol yielded two derivatives of guaiacylglycerol- β -coniferyl ether, each carrying a second aryl ether group in the α -position. If such α -aryl ether structures were present in lignin, their hydrogenolysis would also give rise to the liberation of phenolic hydroxyl, although they might be expected to react very slowly, in analogy to the carbinols and carbinol methyl ethers of similar type (V). On the basis of the finding that the methylation of Björkman lignin with cold $\text{CH}_3\text{OH-HCl}$ did not bring about any significant liberation of phenolic OH , whereas a benzyl aryl ether model (veratryl 2-methoxyphenyl ether) readily suffered methanolysis (Adler, E. and Gierer, J., in Treiber, E., *Die Chemie der Pflanzenzellwand*, Springer-Verlag, Berlin, Göttingen, Heidelberg, 1957, p. 471; and Ref.⁶), it was concluded that benzyl aryl ether linkages are very scarce in lignin.

was made up of dimeric elements of the phenylcoumaran type (IV). By converting the phenylcoumaran elements into phenylcoumarone structures, Adler, Delin and Lundqvist¹³ recently estimated the amount of these elements to be nearly 20 % of the lignin molecule. The latter figure, however, may include "open" dimeric elements of type IVa, which also would yield the phenylcoumarone structure under the experimental conditions used.

On the basis of the results reported above, of the 0.5—0.6 moles of H_2/OCH_3 consumed by the lignin, 0.1—0.2 moles may be attributed to the hydrogenolysis of benzyl alcohol and benzyl ether groupings (including pinoresinol structures) and 0.05 moles to the hydrogenolytic opening of phenylcoumaran structures. As will be shown in the following section, the remainder of the hydrogen consumed may be ascribed in part to the hydrogenation of carbonyl and ethylene groups.

2. Hydrogenation of carbonyl and ethylene groups

As shown in Part II¹, keto groups adjacent to the guaiacyl or veratryl nucleus (α -keto groups) are reduced in the Pd-HCl system, the rate of consumption of the first mole of H_2 (aryl-CO— \rightarrow aryl-CHOH—) being markedly higher than that of the second mole of H_2 (aryl-CHOH— \rightarrow aryl-CH₂—). Coniferyl aldehyde and coniferyl alcohol were readily reduced to dihydroconiferyl alcohol. The occurrence and extent of the corresponding reactions in Björkman lignin have now been examined by $\Delta\epsilon$ methods as introduced by Aulin-Erdtman¹².

In the range above 300 $m\mu$, the ultraviolet absorption of hydrogenated Björkman lignin (Fig. 2, curve *b*, left hand ordinate) was markedly lower than that of untreated Björkman lignin (curve *a*), indicating the loss of chromophores with ethylenic and carbonyl groups conjugated with the aromatic

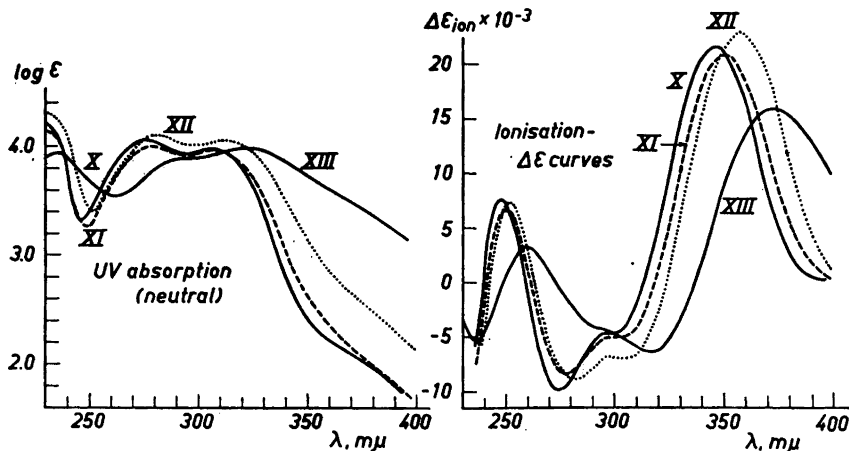
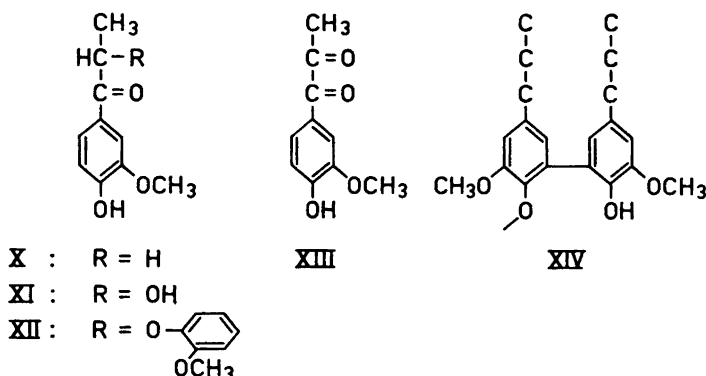


Fig. 3. UV-absorption (in neutral solution) and ionisation- $\Delta\epsilon$ curves of some guaiacyl-propanone models. 4-Propioguiaiacone (X); α -hydroxypropioguiaiacone (XI); α -guaiacoxypropioguiaiacone (XII); vanilloyl methyl ketone (XIII). Neutral solvent, ethanol-water (1:1). Alkaline solvent, 0.1 N NaOH in ethanol-water (1:1).

nuclei. By subtracting the ϵ values of curves *a* and *b* from those obtained for the solutions of the corresponding products in 0.1 N NaOH (which are not included in Fig. 2), the ionisation- $\Delta\epsilon$ curves¹² (Fig. 2, curves *a'* and *b'*) were constructed. In curve *b'*, the long-wave $\Delta\epsilon$ -maximum at 357 $m\mu$ present in *a'* is missing, which indicates that the hydrogenation had resulted in the reduction of α -keto groups of phenolic guaiacyl propane units.

A comparison of the ionisation- $\Delta\epsilon$ curves of a few phenolic α -ketones (Fig. 3) shows that α -guaiacoxy-propioiguaiacone (XII)⁷ gives a $\Delta\epsilon$ -maximum at 357 $m\mu$, *i.e.* at the position characteristic of the corresponding maximum for Björkman lignin, whereas the $\Delta\epsilon$ -maxima for propioiguaiacone (X) and α -hydroxypropioiguaiacone (XI) are found at somewhat shorter wave-length values, and that of vanilloyl methyl ketone (XIII) at a higher wave-length.



The similarity of the absorption curve of catalytically hydrogenated lignin (Fig. 2, curve *b*) with that of a lignin which had been treated with borohydride prior to the hydrogenation (Fig. 2, curve *c*) also supports the view that the conjugated carbonyl groups were reduced by the hydrogenation.

It may also be noted that the ionisation- $\Delta\epsilon$ curve of borohydride-reduced and subsequently hydrogenated lignin (Fig. 2, curve *c'*) still shows a smoothly descending branch above 320 $m\mu$. According to Aulin Erdtman¹², this region of the difference curve is to be attributed to 6,6'-dehydrodiguaiacyl elements (XIV), in which at least one of the two nuclei is phenolic. Comparison of the $\Delta\epsilon$ values of curve *c'* with those of appropriate models¹² indicates that the Björkman lignin examined contained 0.06 6,6'-dehydrodiguaiacyl elements per OCH₃. A similar value has been reported¹² for Brauns lignin.

The difference between the $\Delta\epsilon$ values, at 357 $m\mu$, of curves *a'* and *c'* (Fig. 2) should be a measure of the number of phenolic guaiacyl- α -ketone elements (type VIII, R = H). Based on model substance XII, the difference value (350) would indicate the presence of 0.015 phenolic units VIII per OCH₃ in Björkman lignin. This value is in satisfactory agreement with that obtained previously by means of the borohydride-reduction- $\Delta\epsilon$ method (about 0.01)³.

As shown recently³, the presence of phenolic as well as non-phenolic aryl- α -ketones and coniferyl aldehyde units can be demonstrated by studying the spectral changes occurring when lignin is reduced with sodium borohydride in alkaline solution (" $\Delta\epsilon_r$ curves"). Similar examination of catalytically

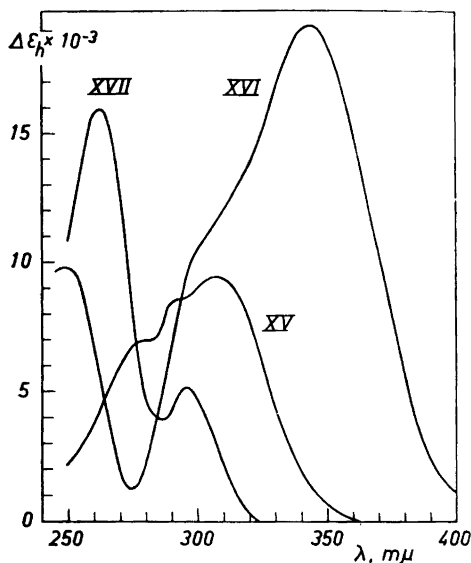


Fig. 4. Hydrogenation- $\Delta\epsilon$ curves of some model compounds. α -Guaiacoxypropioveratrone (XV); isopropylconiferyl aldehyde (XVI); isopropylconiferyl alcohol (XVII). Solvent: 93 % acetic acid. Catalyst: $\text{PdCl}_2\text{-BaSO}_4$.

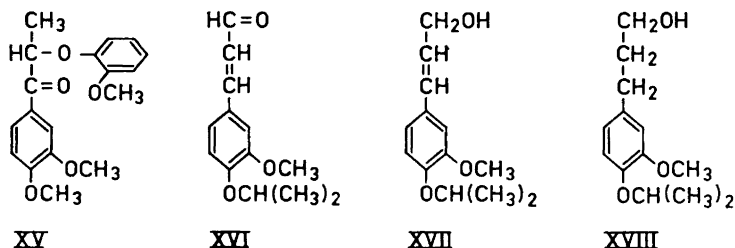
hydrogenated Björkman lignin gave no appreciable decrease of absorption in the wave-length region of 300—400 μ . This shows clearly that not only the phenolic but also the non-phenolic α -ketone and coniferyl aldehyde units, originally present in the lignin, have been hydrogenated. The absence of coniferyl aldehyde groupings in the hydrogenated products is also obvious from the failure of the latter products to give specific colour reactions, *e.g.*, with *p*-aminobenzoic acid³.

Finally, a closer examination of the spectral changes effected by the hydrogenation gave qualitative and quantitative information regarding not only the carbonyl groups but also the ethylenic groupings in Björkman lignin.

In Fig. 4, the spectral changes taking place on catalytic hydrogenation of the conjugated ethylene and carbonyl groups of model substances XV—XVII in 93 % acetic acid are represented as "hydrogenation- $\Delta\epsilon$ curves"¹² (" $\Delta\epsilon_h$ curves").

The $\Delta\epsilon_h$ curve for the unknown isopropylconiferyl alcohol (XVII) was obtained by considering the $\Delta\epsilon_h$ and $\Delta\epsilon_r$ curves for isopropylconiferyl aldehyde (XVI)¹⁴ (see Fig. 4). The $\Delta\epsilon_h$ curve represents the spectral changes involved when both the carbonyl and ethylenic groups are reduced (*i.e.* XVI \rightarrow XVIII). The $\Delta\epsilon_r$ curve (see Ref.³, Fig. 3) represents the spectral change involved when only the carbonyl group is reduced (XVI \rightarrow XVII). The difference between these two curves should approximate the $\Delta\epsilon_h$ curve for XVII. This curve, shown in Fig. 4, is very similar to the $\Delta\epsilon_h$ curve of coniferyl alcohol (*cf.* Aulin-Erdtman and Hegbom^{12b}). Whereas the latter authors presented the hydrogenation difference curves by negative values, the corresponding positive values are used in the present paper.)

In Table 2, the position and height of the maxima of the $\Delta\epsilon_h$ curves of these and two further model compounds are summarised. There was no appreciable difference between the $\Delta\epsilon_h$ maxima for the non-phenolic com-



pounds given in Fig. 4 and Table 2, and the corresponding analogues with a free phenolic hydroxyl group.

Fig. 5 gives the $\Delta\epsilon_h$ curves for two hydrogenations with Björkman lignin, one at atmospheric pressure (Table 1, expt. 1) the other at 4 atmospheres (expt. 5). In spite of the pressure difference, the two experiments yielded similar curves, both curves exhibiting a plateau at 260 $m\mu$, a maximum at 308 $m\mu$ and a shoulder at about 340 $m\mu$. Comparison with the model experiments (Fig. 4) shows that these features are to be attributed to the hydrogenation of C=C bonds conjugated with aromatic rings (model XVII), α -keto groups (model XV), and cinnamaldehyde side-chains (model XVI), respectively. On the basis of the $\Delta\epsilon_h$ values obtained for the models (Fig. 4 and Table 2), the $\Delta\epsilon_h$ values of the lignin curves (Fig. 5) indicate that the following amounts (per OCH_3) of the various chromophores have been hydrogenated:

- 0.03 cinnamyl alcohol groups (type VI)
- 0.03—0.04 cinnamaldehyde groups (type VII)
- 0.05 aryl- α -ketone groups (type VIII)

The number of cinnamyl alcohol groupings (type VI) is in accordance with that estimated by Lindgren and Mikawa¹⁵ by means of a colour reaction. The values for cinnamaldehyde and α -ketone groups are satisfactorily close to those obtained by means of the $\Delta\epsilon_r$ method (0.03—0.04 cinnamaldehyde and 0.06—0.07 α -CO groups)³. It may also be noted that the three figures are

Table 2. Maxima of the "hydrogenation- $\Delta\epsilon$ curves" of some model substances.

Substance	maximum		maximum	
	λ ($m\mu$)	$\Delta\epsilon_h \times 10^{-3}$	λ ($m\mu$)	$\Delta\epsilon_h \times 10^{-3}$
α -Guaiacoxy-propioveratrone (XV) ⁷ (see Fig. 4)	280	7.0	308	9.5
ω -Hydroxy-propioveratrone	273	8.9	305	9.0
Isopropylcinniferyl aldehyde (XVI) ¹⁴ (see Fig. 4)	250	9.8	343	19.3
Isopropylcinniferyl alcohol (XVII) (see Fig. 4)	262	16.0	295	5.1
Dehydrodiisoeugenol ¹²	269	16.5	298	5.0

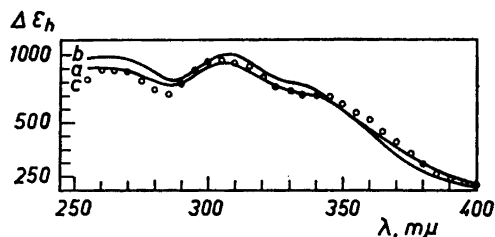


Fig. 5. Hydrogenation- $\Delta\epsilon$ curves of Björkman lignin. Curve *a*: Difference between ϵ values of untreated lignin (cf. $\log \epsilon$ curve *a* in Fig. 2) and ϵ values of lignin solution after 24 h hydrogenation according to Table 1, expt. 1. Curve *b*: Similar difference curve for hydrogenation expt. 5, Table 1. Curve *c*: Calculated for a mixture containing (mole per liter) 0.02 dehydrodiisoeugenol, 0.01 isopropylconiferyl alcohol (XVII), 0.04 ω -hydroxypropioveratrone, 0.01 α -guaiacoxypropioveratrone (XV), 0.03 isopropylconiferyl aldehyde (XVI), 0.003 coniferyl aldehyde. For $\Delta\epsilon_h$ values of the model substances see Fig. 4 and Table 2.

reasonably close to the corresponding values obtained by Aulin-Erdtman¹² for Brauns lignin.

A "synthetic" $\Delta\epsilon_h$ curve was constructed by summation of the $\Delta\epsilon_h$ values for suitable amounts of model compounds, as given in the legend to Fig. 5. This curve (*c*) follows rather closely the $\Delta\epsilon_h$ curves for Björkman lignin, which indicates that the interpretation of the latter curves and the choice of the model compounds in calculating the quantities of the various components was correct.

Evidently, the figures given above for the amounts of the chromophores VI—VIII in Björkman lignin can be reliable only if their hydrogenation has been complete. As shown by Fig. 6, this is actually the case. The curves represent the decrease of absorption, during the course of a hydrogenation experiment, at three different wave-lengths which are close to the $\Delta\epsilon_h$ maxima characteristic of the three chromophore structures. Obviously, the hydrogenation of these structures approaches its end point within a period of 4—5 h.

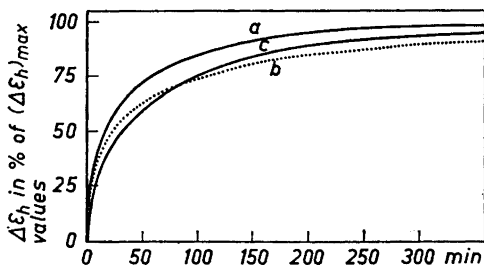


Fig. 6. Rate of hydrogenation of chromophores of Björkman lignin. Decrease of absorption at 270 $m\mu$ (*a*), 310 $m\mu$ (*b*) and 350 $m\mu$ (*c*). Reaction mixture: 0.3 g lignin, 1.5 g $\text{PdCl}_2 \cdot \text{BaSO}_4$, 50 ml of 93% HOAc, H_2 at atmospheric pressure; room temperature. Extinction was measured in centrifuged samples and the $\Delta\epsilon$ values obtained expressed as % of final $\Delta\epsilon_h$, attained after 24 h hydrogenation.

The sum of cinnamaldehyde groups (type VII, 0.03—0.04 per OCH_3) and aryl- α -ketonic groupings (type VIII, 0.05 per OCH_3), determined as above, gives a total of 0.08—0.09 conjugated carbonyl groups per OCH_3 . It represents somewhat less than half of all the carbonyl groups (about 0.20 CO/OCH_3) previously³ found to be present in Björkman lignin by oximation. By the latter method, the catalytically hydrogenated lignin preparations (Table 1, expts. 1 and 5) were found to contain a residual number of 0.07 carbonyl groups per OCH_3 . They can be assumed to be β -keto groups (IX), which in the model experiments¹ were found to be reduced extremely slowly, and which cannot be determined by the $\Delta\varepsilon_{\text{h}}$ method. Spectrochemical examination of lignin hydrogenation combined with the oximation of the hydrogenated lignin has thus revealed the presence of $0.09 + 0.07 = 0.16$ CO groups per OCH_3 . The difference, *i.e.* $0.20 - 0.16 = 0.04$ CO/OCH_3 , seems to be attributable to a fraction of the original amount of 0.10 β -keto groups³, which has undergone hydrogenation.

The results regarding the various types of carbonyl groups reported above agree well with those obtained by means of the spectrochemical borohydride reduction and the oximation methods³. Gierer and Söderberg¹⁸, on the basis of a volumetric borohydride reduction method, however, concluded that Björkman lignin contains a total of 0.41—0.44 CO/OCH_3 , or twice the amount found by oximation (0.20). Since the number of conjugated CO groups now seems to be definitely limited to about 0.1 CO/OCH_3 , the existing discrepancy might be supposed to be due to a failure of the oximation method in the determination of the isolated (β -)keto groups. As will be shown in the subsequent paper¹⁷, however, the values obtained with the volumetric borohydride method under the conditions used by Gierer and Söderberg are too high. Support for this conclusion is also to be found in the results of hydrogenations with a nickel boride catalyst, part B of this paper.

B. HYDROGENATION OF BJÖRKMAN LIGNIN OVER A NICKEL BORIDE CATALYST

Model experiments¹ revealed that the nickel boride catalyst of Paul *et al.*¹⁸ shows decreasing activity in the hydrogenation of the following series: $\text{C}=\text{C} > \beta\text{-CO groups} > p\text{-alkoxyaryl ketones} > p\text{-hydroxyaryl ketones} > \text{aryl carbinols}$. The ethylene groups were rapidly hydrogenated whereas the aryl carbinols were practically inert. The selectivity of the alkaline nickel boride system was rather different from that of the acidic Pd system. The $\beta\text{-CO}$ groups, while largely resistant to hydrogenation over the Pd catalyst, were readily reduced in the presence of the boride catalyst. Conversely, aryl carbinols reacted with hydrogen when Pd was the catalyst but not when nickel boride was used.

When an alkaline solution of Björkman lignin was hydrogenated in the presence of the nickel boride catalyst, about 0.20 moles of H_2 per OCH_3 were consumed during 30 min., and the reaction practically ceased after 4—5 h, when 0.28 moles of H_2/OCH_3 had been consumed (Fig. 1, curve *b*).

UV and IR examination of the recovered hydrogenation product showed that the ethylenic bonds as well as the majority of the carbonyl groups had been reduced. Only about 0.01 phenolic aryl keto groups and traces of non-phenolic aryl keto groups (VIII, R = H or C) survived. The quinone monochlorimine colour reaction according to Gierer¹⁹ was still positive, indicating that the phenolic aryl carbinol groupings (I, R = R' = H) had not been affected. On treatment with methanolic hydrochloric acid at 20°, the hydrogenated product acquired 0.43 new OCH₃ groups per OCH₃ originally present, which is in harmony with the expectation that the benzyl alcohol and benzyl ether groupings would not undergo hydrogenolysis (*cf.* Ref.⁶).

Similar methylation introduces 0.56 OCH₃ (mean value) into untreated Björkman lignin, and 0.50 OCH₃ into borohydride-reduced Björkman lignin. The difference between these two figures may be due to the borohydride reduction of the ω -hydroxyguaiacylacetone structure, which may occur in lignin (the presence of about 0.1 β -keto groups has been demonstrated³) and which, in model experiments, was shown to undergo methylation. On hydrogenation over nickel boride these groups will also be reduced, but, in addition, coniferyl alcohol side-chains, which also react with CH₃OH—HCl^{6,7}, will be saturated and thus be made resistant to methylation. In NaBH₄-lignin there will be present 0.03 original coniferyl alcohol groups (see p. 379) and a further 0.03—0.04 formed by reduction of coniferyl aldehyde groups. These relationships would explain the fact that the methylation of H₂/Ni boride-reduced lignin introduces 0.07 fewer methoxyl groups than the methylation of NaBH₄-reduced lignin. The 0.43 methylatable groups present in the former material then would mainly be aryl carbinol (ether) groupings.

In accordance with the hydrogenation experiments in the Pd—HCl system, the results obtained in the alkaline nickel boride system indicate that the sum of ethylenic and carbonyl groups in Björkman lignin does not exceed a value of 0.30 per OCH₃. Since the number of ethylenic groups is 0.06—0.08 (*i.e.*, 0.03—0.04 each present in cinnamaldehyde and in cinnamyl alcohol residues, *cf.* also Ref.¹⁵), the total amount of carbonyl groups is found to be 0.22—0.24 per OCH₃. This figure is close to the value of 0.20 total CO/OCH₃ previously found³ by the oximation method.

EXPERIMENTAL

Björkman lignin (= "milled wood lignin", "M.W. lignin") was obtained from Norway spruce (*Picea abies*)²⁰.

Sodium borohydride-reduced Björkman lignin was prepared according to the procedure given by Adler, Hernestam and Walldén², with a few modifications. The lignin (3 g, OCH₃ 15.23 %) was suspended in aqueous ethanol (1:1, 180 ml) and dissolved by the addition of 0.1 N sodium hydroxide (50 ml). Sodium borohydride (1.2 g) was added in portions. The initially red-brown colour of the solution slowly became a light yellow. Further portions of 0.1 g of sodium borohydride were added each of the following four days. The pH was adjusted to 4 with aqueous hydrochloric acid and the mixture was evaporated to dryness under reduced pressure. The residue was four times suspended in water and recovered by centrifuging. After four such washings it was dried in vacuum over P₂O₅ and NaOH. The light tan powder (2.6 g) was dissolved in 50 ml of a mixture of 1,2-dichloroethylene, abs. ethanol and dioxan (2:1:1); traces of undissolved material were removed by centrifugation. The solution was poured into 500 ml of a mixture of ether and petroleum ether (1:1), the lignin precipitate centrifuged off, washed twice with the latter solvent mixture and finally with petroleum ether. After drying in a stream of warm air, a cream coloured powder (2.5 g = 83 %; CH₃O 15.34 %) remained.

The preparation of the *catalysts* and the *hydrogenation procedure* have been described in the preceding paper¹. For the experiments to Fig. 5, the reaction vessel was provided with a side-tube, which was covered by a rubber membrane. Samples were withdrawn from the reaction mixture by a syringe inserted through the rubber membrane. Experiments 5 and 6 (Table 1) were carried out in a Parr low pressure hydrogenation apparatus.

Isolation of the hydrogenated lignin products. a) *After hydrogenation over Pd-BaSO₄.* The catalyst was centrifuged off and washed with acetic acid, the washings being combined with the solution. The solvent was removed under reduced pressure (bath temp. not exceeding 45°). The residue was redissolved in 93 % acetic acid (5 ml for 0.1 g of lignin) and the solution was filtered and allowed to drop into a fifteenfold volume of water. The lignin precipitate was centrifuged off, washed with water and dried in a vacuum desiccator over P₂O₅ and NaOH. This material was dissolved in a mixture of 1,2-dichloroethylene and ethanol (2:1), reprecipitated by pouring the filtered solution into ether-petroleum ether (1:1) and washed and dried as described for the NaBH₄-lignin. Yield 90 %.

b) *After hydrogenation over nickel boride.* The centrifuged alkaline reaction mixture was acidified to pH 4 with hydrochloric acid, ethanol was removed under reduced pressure, and the lignin residue purified as above.

Methylation of Björkman lignin with methanolic hydrochloric acid. A solution of the lignin (150 mg) in abs. dioxan (15 ml) was mixed with 0.3 N methanolic hydrochloric acid (15 ml). After four days at room temperature the mixture was brought to pH 4 with 0.6 N methanolic sodium hydroxide, neutralised by the addition of a little solid sodium bicarbonate and evaporated under reduced pressure. The residue was kept for one day in a vacuum desiccator over P₂O₅, the lignin was dissolved in abs. dioxan (10 ml), and reprecipitated by pouring the filtered solution into ether-petroleum ether (1:1, 120 ml). The lignin was washed and dried as described above. Yield, 120–140 mg, ash content about 1 %.

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