

Carbonyl Groups in Lignin

II*. Catalytic Hydrogenation of Model Compounds Containing Aryl Carbinol, Aryl Carbinol Ether, Ethylene and Carbonyl Groups**

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The catalytic hydrogenation of a variety of lignin model compounds containing aryl carbinol, aryl carbinol ether, ethylene and carbonyl groups has been examined. In a reaction mixture containing 93 % acetic acid as a solvent, Pd-BaSO₄ as a catalyst and HCl as a promoter, hydrogenolysis of the aryl carbinols I and their methyl ethers proceeded readily, but the rate of reaction was decreased if the β - and γ -positions of the propane side-chain were substituted by hydroxyl groups. Further inhibition was produced by a β -guaiacoxy substituent and especially by the simultaneous presence of a β -guaiacoxy and a γ -hydroxy substituent (guaiacylglycerol- β -guaiacyl ether type). Cyclic benzyl ethers, as in pinoresinol or in phenylcoumarans, were readily opened by hydrogenolysis.

Ethylenic bonds, either conjugated with the aromatic ring (as in coniferyl alcohol) or isolated (as in eugenol) were rapidly saturated.

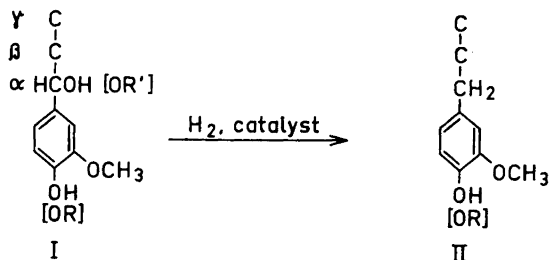
Keto groups conjugated with the aromatic ring (α -keto groups) were reduced at satisfactory rates. In coniferyl aldehyde both the carbonyl and the ethylenic group were rapidly hydrogenated. Isolated keto groups (β -keto groups), however, reacted extremely slowly.

In a few experiments a nickel boride catalyst and an alkaline solvent were used. In this system the rate of hydrogenation decreased in the following series: C = C > β -CO groups > α -CO groups. No appreciable hydrogenolysis of aryl carbinols and aryl carbinol ethers took place.

The original purpose of the investigations reported in the present and the following paper was the conversion, by catalytic hydrogenolysis, of the aryl carbinol and aryl carbinol ether groups (I) of Björkman lignin into groupings of type II. The presence of the groupings of type I in lignin was suggested

* Part I, see Ref.^{16a}

** Preliminary communication, Marton, J., Tionde Nordiska Kemistmötet, Stockholm, 1959, Abstracts of Papers, *Svensk Kem. Tidskr.* 71 (1959) 439.



by B. Holmberg and is supported by numerous arguments based on model studies as well as by analytical results and enzymatic syntheses (for literature, see Refs.^{1,2}). It seemed that a detailed study of the hydrogenolysis of these groups might give new information on their occurrence and frequency in lignin and on the relative proportion of the various types indicated in formula I (free or etherified hydroxyl groups). Furthermore, the reductive removal of the highly reactive benzyl alcoholic hydroxyl groups would greatly reduce the tendency of lignin to undergo condensation reactions under the influence of acid or alkali, and a lignin product containing groups of type II instead of type I should therefore be a suitable starting material for degradation experiments.

Mild catalytic hydrogenation of lignin would also involve the reduction of ethylenic and carbonyl groups present, and therefore, in an investigation of the hydrogenation reaction, the changes brought about by the latter reactions would have to be taken into consideration. As will be shown in the following paper, hydrogenolysis of benzyl alcohol and ether groupings in lignin was only partially successful. On the other hand a study of the simultaneous reduction of ethylenic and carbonyl groups provided valuable structural information, and therefore the hydrogenation work is reported in this series of papers on "Carbonyl Groups in Lignin".

The present publication describes hydrogenation experiments with various lignin model compounds, mainly of the guaiacyl- and veratrylpropane type, containing aryl carbinol, aryl carbinol ether, ethylene, and carbonyl groups.

In order to avoid unwanted hydrogenation of the aromatic nuclei, the experiments were carried out under mild conditions, *i.e.*, at room temperature and ordinary pressure. In view of the solubility properties of Björkman lignin, acetic acid containing 7 % of water was chosen as a solvent for the model compounds. Palladium chloride on barium sulphate (5 % PdCl₂), prehydrogenated in the solvent immediately before the addition of the substrate, was found to be a highly active and suitable catalyst.

The activity of the freshly reduced catalyst (preparation, see Exptl.) in 93 % acetic acid was greater than that of the commonly used palladium or platinum catalysts (*cf.*, *e.g.*, Ref.³). This is evidently due to the presence of the hydrochloric acid formed in the prehydrogenation. The hydrochloric acid also catalysed a more or less complete acetylation of the non-reducible alcoholic hydroxyl groups present in a number of the model substances studied (as well as in lignin) (*cf.* also Ref.⁴). This side-reaction could be suppressed by the addition of sodium acetate but the activity of the catalyst was decreased at the same time. If the PdCl₂-BaSO₄ catalyst after hydrogenation was washed until free from HCl, as generally recommended³, before being added to the reaction mixture, its

activity was considerably diminished, and the original activity was not restored on subsequent addition of hydrochloric acid. For instance, hydrogenolysis of benzyl alcohol with the acid-free prehydrogenated catalyst was eight times slower than with the catalyst prehydrogenated *in situ*, *i.e.*, with the promoting hydrochloric acid present, as used here. Addition of HCl or HClO₄ to the system containing the prehydrogenated and washed catalyst only restored the activity to about 50 % of that obtained without washing after prehydrogenation. This indicates that washing changes the surface structure of the catalyst.

Methylcellosolve and dioxan, which are good solvents for Björkman lignin, were used in some model experiments instead of 93 % acetic acid. In methylcellosolve, the rate of hydrogenolysis of aryl carbinols was usually lower than in the acetic acid. Dioxan could not be used, as it dissolved the palladium chloride; subsequent prehydrogenation produced a palladium precipitate with very slight activity.

Platinum on asbestos showed little activity in the hydrogenolysis of most of the guaiacyl carbinols studied.

A few hydrogenation experiments were carried out in an alkaline medium in the presence of the nickel boride catalyst described by Paul *et al.*⁵ This system was of special interest in view of the solubility of lignin in dilute alkali.

HYDROGENOLYSIS OF THE BENZYL-OXYGEN LINKAGE

Although numerous benzyl alcohols and benzyl ethers have been subjected to hydrogenolysis⁶, very little is known about the reactivity of compounds of the guaiacyl ethyl carbinol type (structure I) characteristic of lignin. In a short communication, Japanese workers⁷ have recently reported some experiments with C₆-C₂ compounds, showing that, as expected, only hydroxyl groups in the benzyl position are reduced.

In the present work, an examination was first made of the guaiacyl and veratryl ethyl carbinols III—X which formed suitable models for two of the possible variants of structure I, *i.e.*, the free carbinols with a free phenolic hydroxyl and with an etherified phenolic hydroxyl. For comparison, some experiments were carried out with benzyl alcohol and with vanillyl and veratryl

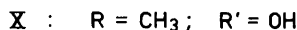
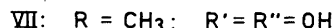
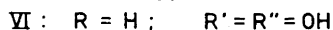
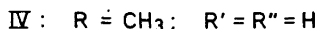
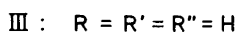
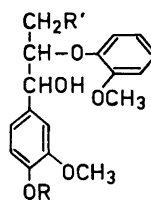
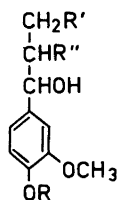


Table 1. Hydrogenolysis of aryl carbinols. Catalyst: PdCl₂-BaSO₄. Solvent: 93% acetic acid.

Substance	Amount of substance, mmole	Amount of catalyst, g	Time required for consumption of 0.5 mole of H ₂ per mole of substance, t _{1/2} (min)
Benzyl alcohol	1	0.05	1.5
	1	0.1	1
Vanillyl alcohol	1	0.05	4.5
	1	0.1	2
Veratryl alcohol	1	0.05	9
	1	0.1	2
Ethyl guaiacyl carbinol (III)	{ 1	0.1	16
	{ 1	0.2	3.5 ^a
	{ 1	0.5	1.5 ^b
Ethyl veratryl carbinol (IV)	1	0.1	3 ^a
Methylisoeugenolglycol (V), α -form ^{a,c}	{ 0.5	0.2	94
	{ 0.5	0.5	47
Methylisoeugenolglycol (V), β -form ^{a,c}	{ 0.5	0.2	64
	{ 0.5	0.5	25 ^b
Guaiacylglycerol (VI), m.p. 83–84° ^{a,d}	0.5	0.5	32 ^b
Veratrylglycerol (VII), m.p. 109–110° ^{a,c}	0.5	0.5	33
Isoeugenolglycol- β -guaiacyl ether (VIII) ¹⁰	{ 0.5	0.2	77
	{ 0.5	0.5	50
Methylisoeugenolglycol- β -guaiacyl ether (IX)	{ 0.5	0.2	130
	{ 0.5	0.5	76 ^b
Veratrylglycerol- β -guaiacyl ether (X) ¹¹	0.5	0.5	140 ^{b,f}

^a For further details of this experiment, see Experimental.

^b See also Fig. 1.

^c It has been shown²⁴ that the α -form^a is the D,L-*erythro* isomer, the β -form the D,L-*threo* isomer of V.

^d It has been shown²⁴ that the crystalline form of guaiacylglycerol, m.p. 83–84°, is the D,L-*erythro* isomer.

^e It has been shown²⁴ that the veratrylglycerol isomer of m.p. 109–110° is the D,L-*threo* isomer.

^f Reduction incomplete after 24 h.

alcohols. The results are summarised in Table 1, in which the rates of hydrogenolysis are expressed as the time $t_{1/2}$ (min) required for the uptake of 0.5 mole of hydrogen per mole of substance. The total hydrogen uptake in most cases was close to the expected 1 mole of hydrogen per mole. Hydrogenation curves for several of these compounds are shown in Fig. 1.

The results obtained show that substituents at the β and γ positions in the propane side-chain had a marked effect on the rate of hydrogenolysis. This can be illustrated by the following examples. Using 0.1 g of the PdCl₂-BaSO₄ catalyst and 1 mmole of ethyl veratryl carbinol (IV) in 15 ml of the solvent, 1 mole of hydrogen was consumed in about 40 min, $t_{1/2}$ being 3 min. (4-Propyl-

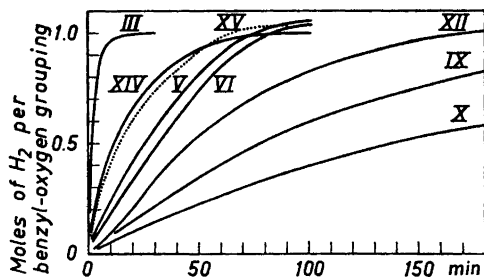


Fig. 1. Hydrogenolysis of some aryl carbinols and aryl carbinol ethers. Experimental conditions, see Tables 1 and 2. Substances see p. 359 and below.

veratrol was recovered from the reaction mixture.) The presence of a hydroxyl group in the β -position (methylisoeugenol glycol, V, β -form⁸) caused the hydrogenolysis of the α -hydroxyl group to proceed at a considerably lower rate, $t_{1/2}$ being 25 min, even though a greater amount of catalyst was used than in the hydrogenolysis of IV described above. An additional hydroxyl substituent in the γ -position (veratrylglycerol, VII⁹) caused a further slight decrease in the rate of hydrogenolysis. Considerable inhibition of hydrogenolysis was caused by a guaiacoxy substituent in the β -position (IX¹⁰, $t_{1/2}$ = 76 min), and hydrogenolysis was extremely slow, when the β -carbon atom carried a guaiacoxy group and the γ -carbon atom a hydroxyl group (veratrylglycerol- β -guaiacyl ether, X¹¹, $t_{1/2}$ = 140 min).

There was no marked difference in the rates of hydrogenolysis of the veratryl compounds and their phenolic (guaiacyl) analogues (see Table 1 and Fig. 1).

Experimental evidence has been given¹² for the view that one fourth to one third of the arylpropane units of lignin are of the guaiacylglycerol- β -aryl ether type (*cf.* model compound X). On the basis of the model experiments

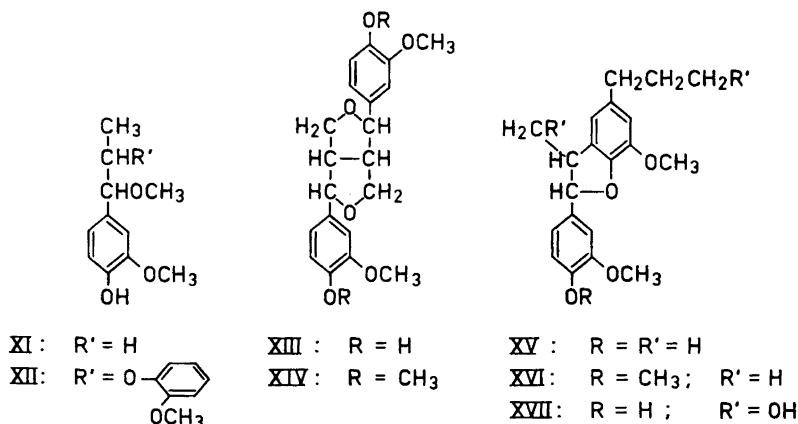


Table 2. Hydrogenolysis of aryl carbinol ethers. Catalyst: PdCl₂-BaSO₄. Solvent: 93 % acetic acid.

Substance	Amount of substance, mmole	Amount of catalyst, g	Time required for consumption of 0.5 mole of H ₂ per mole of substance, t _{1/2} (min)
Diveratryl ether ¹³	0.5	0.05	8.5
	0.5	0.1	2
Ethyl guaiacyl carbinol - <i>α</i> -methyl ether (XI) ²⁴	1	0.05	27
	1	0.1	10
	1	0.2	2.5 ^a
<i>Isoeugenolglycol-α</i> -methyl- <i>β</i> -guaiacyl ether (XII) ¹⁰	0.5	0.5	45 ^b
	0.5	0.2	22 ^c
Pinoresinol (XIII)			91 ^d
	0.5	0.1	30 ^c
			101 ^d
	0.5	0.2	15 ^c
			50 ^d
Pinoresinol dimethyl ether (XIV)	0.5	0.5	4 ^c
			14 ^{d,b}
			61
Dihydro-dehydrodi <i>iso</i> -eugenol (XV)	1	0.2	36
	0.5	0.2	14 ^b
	0.5	0.5	14 ^b
Dihydro-dehydrodi <i>iso</i> -eugenol methyl ether (XVI)	0.5	0.2	47
Dihydro-dehydrodicoumaronyl alcohol (XVII)	0.5	0.2	23

^a For further details of this experiment, see Experimental.

^b See also Fig. 1.

^c t_{1/2} for the consumption of the first mole of hydrogen per mole of substance.

^d t_{1/2} for the consumption of the second mole of hydrogen per mole of substance.

reported above, it can therefore be predicted that the hydrogenolysis of a considerable proportion of the aryl carbinol groups present in lignin will be extremely slow.

Substances XI—XVII and diveratryl ether ¹³ were investigated as model compounds for the aryl carbinol ether groupings postulated in lignin (*cf.* formula I, with OR' or with OR and OR', R and R' being C-atoms of the propane side-chains in adjacent monomers) (Table 2 and Fig. 1). The calculated amount of hydrogen (1 mole of H₂ per benzyl ether group) was consumed in all cases, and the rate of the reaction was similar to that found for the corresponding model compound with a free carbinol group (*e.g.* the pairs III, XI and VIII, XII). The presence of a guaiacoxy substituent in the *β*-position (XII) again caused a very marked inhibition. Hydrogenolysis of the cyclic benzyl alkyl ether linkages present in pinoresinol (XIII) and its dimethyl ether (XIV) and of the cyclic benzyl aryl ether bonds of the phenylcoumaran derivatives XV, XVI, and XVII proceeded with remarkable ease, if sufficient catalyst was used (*cf.* the low rate of hydrogenolysis of XV and XVI with Pd-black in glacial acetic acid previously reported ¹⁴).

HYDROGENATION OF ETHYLENE GROUPS

In view of the fact that ethylenic linkages are present in lignin, albeit only in small amount (see the following communication), a few unsaturated model compounds were subjected to hydrogenation under the conditions described above (Table 3).

Table 3. Hydrogenation of ethylene groups. Catalyst: PdCl₂·BaSO₄. Solvent: 93 % acetic acid.

Substance	Amount of substance, mmole	Amount of catalyst, g	Time required for consumption of 0.5 mole of H ₂ per mole of substance, t _{1/2} (min)
Eugenol	1	0.1	2
Dehydrodiisoeugenol (XVIII)	2	0.2	1 ^a
Coniferyl alcohol (XIX)	1	0.2	1
<i>α</i> -(2-Methoxy-4-methylphenoxy)-coniferyl alcohol (XX) ²⁶	0.25	0.1	1.5
Dehydrodiconiferyl alcohol (XXI)	0.5	0.2	0.5 ^a

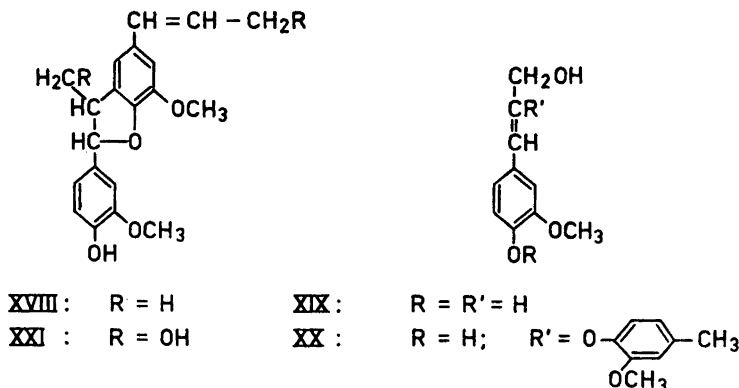
^a Refers to the consumption of the first mole of hydrogen (reduction of the ethylenic bond); a second mole of hydrogen (hydrogenolysis of the furan ring) was consumed at a much lower rate (*cf.* XV and XVII in Table 2).

Eugenol, a model for possible structures containing isolated ethylenic bonds, was rapidly hydrogenated as were double bonds conjugated with the aromatic ring in compounds XVIII—XXI. Because of this rapid C=C hydrogenation, the cinnamyl alcohols XIX—XXI, although they are vinylogous benzyl alcohols, did not undergo hydrogenolysis at the carbinol group. The phenylcoumaran derivatives (XVIII, XXI), after the rapid hydrogenation of the unsaturated side-chain, consumed further hydrogen at a low rate due to hydrogenolysis of the dihydrofuran ring (*cf.* above).

The solvent-catalyst system used in this work has been found to be very suitable for the preparation¹⁵ of dihydrodehydrodiconiferyl alcohol (XVII) from XXI; sodium acetate was added as a buffering agent, thus preventing acetylation of the alcoholic hydroxyl groups which would otherwise be catalysed by the hydrochloric acid formed in the prehydrogenation of the catalyst. Although the rate of hydrogenation was somewhat lower in the presence of sodium acetate, the conversion XXI → XVII was complete in 5 min.

HYDROGENATION OF CARBONYL GROUPS

The carbonyl groups in lignin include (1) aldehyde groups in structures of the coniferyl aldehyde type, (2) keto groups conjugated with the aromatic ring and (3) isolated keto groups (in the β -position of the propane side-chain). The results obtained with models for these types of carbonyl-containing lignin



structures are given in Table 4. Hydrogenation curves for some of these compounds are shown in Fig. 2.

Coniferyl aldehyde (XXII) and its methyl ether (XXIII) were readily hydrogenated, 2 moles of hydrogen being consumed at a nearly constant rate. This indicates that hydrogenation of the ethylenic bond and the carbonyl group proceeded simultaneously at approximately equal rates, with the formation of dihydroconiferyl alcohol (*cf.* below).

Hydrogenation of the conjugated aryl ketones (XXIV—XXXIV) involves reduction to the corresponding aryl carbinol, followed by hydrogenolysis. Both steps proceeded with great ease in the case of 4-propioiguaiacone (XXIV) and its methyl ether (XXV). A hydroxyl group on the terminal carbon atom of the side-chain had some inhibiting effect (β -hydroxypropioveratrone, XXVI). The presence of a hydroxyl substituent on the carbon atom adjacent to the keto group (XXVII, XXVIII) did not inhibit the first step, but caused the second step to proceed at a markedly lower rate, as expected from the behaviour of the glycols V and VI (see Table 1). Ethoxy, acetoxy, and guaiacoxo substituents adjacent to the keto group (XXIX—XXXIII) caused some inhibition of the first step, and the combination of guaiacoxo and hydroxyl substituents, as in XXXIV, produced further inhibition. In general, however, the reduction of the conjugated keto groups proceeded more easily than the subsequent hydrogenolysis of the carbinol groups formed.

The reduction of isolated keto groups (in XXXV—XXXVII) proved to be extremely difficult. Thus, the α -keto groups of the diketones XXXVIII and XXXIX were readily reduced to $-\text{CH}_2-$, but the β -keto groups remained practically unaffected. (The guaiacylacetone and veratrylacetone formed were identified with authentic material by comparison of the infrared spectra.)

It may be of interest to note that, in contrast to their resistance to catalytic hydrogenation, β -keto groups are rapidly reduced by sodium borohydride. Furthermore, while the catalytic hydrogenation of α -keto groups was comparatively easy in both guaiacyl and veratryl compounds, borohydride reduction of the phenolic α -ketones has been found¹⁶ to proceed much more slowly than the reduction of the non-phenolic α -ketones.

Table 4. Hydrogenation of carbonyl compounds.

Substance	Amount of substance, mmole	Amount of catalyst, g	$t_{1/2}$ (min) for consumption, per mole of substance, of	
			1st mole of H_2^a	2nd mole of H_2^b
Vanillin	1	0.1	1.5	1.5
Veratraldehyde	1	0.1	1.5	2
Coniferyl aldehyde (XXII)	0.5	0.1	1.5	1.5 ^c
Methylconiferyl aldehyde (XXIII)	0.5	0.1	1.5	1.5
4-Propioguaiacone (XXIV)	0.5	0.2	1	2 ^d
4-Propioveratrone (XXV)	0.5	0.2	1.5	2.6 ^d
β -Hydroxypropioveratrone (XXVI) ²⁷	0.5	0.2	4	7.5 ^c
α -Hydroxypropio- guaiacone (XXVII) ²⁷	0.5	0.5	1	21
α -Hydroxypropio- veratrone (XXVIII) ²⁷	0.5	0.5	1	88
α -Ethoxypropio- guaiacone (XXIX) ²⁷	0.25	0.2	7	73
α -Ethoxypropio- veratrone (XXX) ²⁷	0.5	0.5	14	65
α -Acetoxyprio- veratrone (XXXI) ²⁷	0.5	0.5	8.5	60
α -Guaiacoxyprio- guaiacone (XXXII) ¹⁰	0.5	0.5	5.5	28 ^c
α -Guaiacoxyprio- veratrone (XXXIII) ¹⁰	0.5	0.5	7.5	56 ^c
α -Guaiacoxyprio- β -hydroxypropio- veratrone (XXXIV) ¹¹	0.5	0.5	51	110 ^c
Guaiacylacetone (XXXV) ²⁷	0.5	0.5	250 ^e	—
Veratrylacetone (XXXVI) ²⁷	0.5	0.5	250 ^e	—
ω -Hydroxy- guaiacylacetone (XXXVII) ²⁷	0.5	0.5	e, c	—
Vanilloyl methyl ketone (XXXVIII) ²⁷	0.5	0.2	0.5	3
Veratroyl methyl ketone (XXXIX) ²⁷	0.5	0.2	1	4

^a Reduction of carbonyl group to carbinol group.

^b Hydrogenolysis of aryl carbinol group formed in the first step; for XXII and XXIII, however, see text, p. 364.

^c See also Fig. 2.

^d See also Experimental.

^e Reaction incomplete after 24 h.

SOME EXPERIMENTS WITH A NICKEL BORIDE CATALYST

The results of reductions using the nickel boride catalyst of Paul *et al.*⁵ are shown in Table 5. As expected, ethylenic bonds (XIX, XL) were readily reduced. Hydrogenation of keto groups however, proceeded slowly, and hydrogenolysis of aryl carbinols was extremely slow. It was therefore possible to obtain ethyl veratryl carbinol (IV) by hydrogenation of vinyl or ethynyl veratryl carbinol (XL, XLI). Thus, unlike the palladium-HCl system, the nickel boride-alkali system showed a marked selectivity with the three types of groupings investigated. There were also differences in the activity of the two hydrogenation systems in the reduction of different carbonyl compounds; with nickel boride an isolated keto group (XXXVI) was more easily reduced than a conjugated keto group while the palladium catalyst showed a reversed sequence of activity.

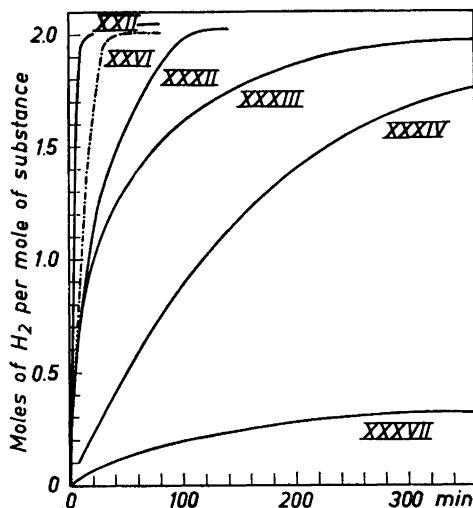


Fig. 2. Catalytic hydrogenation of some carbonyl-containing lignin model compounds. Experimental conditions, see Table 4. Substances see p. 367.

Dihydroconiferyl alcohol (XLII), m.p. 63° (65° according to Semetskina and Shorigina¹⁷), was obtained by hydrogenation of coniferyl alcohol over nickel boride. Hydrogenation of veratrylacetone (XXXVI) gave veratrylpropanol-2 (XLIII), m.p. 40°.

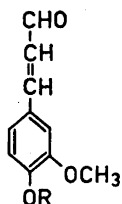
Table 5. Hydrogenation of some model compounds in the presence of a nickel boride catalyst. Reaction mixture: 1 mmole of substance, about 0.2 g of catalyst (see Experimental), 15 ml of ethanol (or aqueous ethanol, 1:1, in the case of phenolic compounds), 0.5 ml of 1 N aqueous NaOH. Atmospheric pressure, room temperature.

Substance	Time required for consumption of 0.5 mole of H ₂ per mole of substance, $t_{1/2}$ (min)
Vinyl veratryl carbinol (XL)	4
Coniferyl alcohol (XIX)	5 ^a
Ethynyl veratryl carbinol (XLI)	18 ^{a,b}
Veratrylacetone (XXXVI)	23 ^a
β -Hydroxypropioveratrone (XXVI)	45
4-Propioguuaiacone (XXIV)	80
α -Guaiacoxypropioguuaiacone (XXXII)	360
Benzyl alcohol	150
Ethyl veratryl carbinol (IV)	c

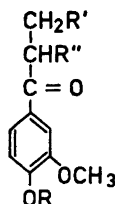
^a See also Experimental.

^b Refers to the consumption of the first mole of hydrogen; a second mole was consumed at a similar rate.

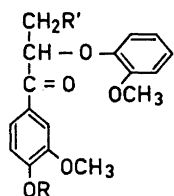
^c Only 0.1 mole of H₂ per mole of IV had been consumed after 360 min.



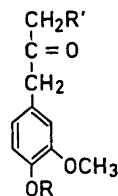
XXII : R = H
XXIII : R = CH₃



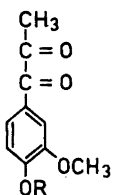
XXIV : R = R' = R'' = H
XXV : R = CH₃; R' = R'' = H
XXVI : R = CH₃; R' = OH; R'' = H
XXVII : R = R' = H; R'' = OH
XXVIII : R = CH₃; R' = H; R'' = OH
XXIX : R = R' = H; R'' = OC₂H₅
XXX : R = CH₃; R' = H; R'' = OC₂H₅
XXXI : R = CH₃; R' = H; R'' = OCOCH₃



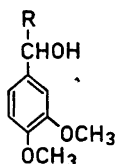
XXXII : R = R' = H
XXXIII : R = CH₃; R' = H
XXXIV : R = CH₃; R' = OH



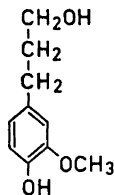
XXXV : R = R' = H
XXXVI : R = CH₃; R' = H
XXXVII : R = H; R' = OH



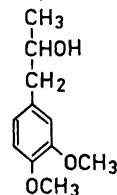
XXXVIII : R = H
XXXIX : R = CH₃



XL : R = CH = CH₂
XLI : R = C ≡ CH



XLII



XLIII

EXPERIMENTAL

PdCl₂-BaSO₄ Catalyst. Barium sulphate was prepared as described by Mozingo³. Palladium chloride (2 g) was dissolved in 12 % aqueous hydrochloric acid (15 ml) by

heating for about 1 h on a steam bath. The solution was added to a paste of barium sulphate (22 g) and distilled water (17 ml), and after thorough stirring the mixture was slowly taken to dryness on a steam bath. The product, which should have a uniform brown colour, was dried at 105°. When stored in a dark bottle, its activity remained unchanged for several months. The product was powdered before use.

Hydrogenation procedure. Hydrogenation of the lignin model compounds was carried out at room temperature and atmospheric pressure in a semi-micro apparatus, which was a modification of that described by Frampton *et al.*¹⁸

The catalyst (0.05–0.5 g) was suspended in 10 ml of acetic acid containing 7 % of water, and hydrogenated (about 30 min), before adding the substrate (0.5–2 mmole) dissolved in 5 ml of the same solvent. A magnetic stirrer was used.

Nickel boride catalyst containing chromium boride as a promoter was prepared according to Paul *et al.*⁵ The catalyst, stored under ethanol, lost its activity in a few days.

For the hydrogenation experiments (see Table 5), the ethanol was decanted and 0.2 g of the wet catalyst was added to a mixture of 10 ml of ethanol (ethanol-water 1:3, in the hydrogenation of phenolic substances) and 0.5 ml of 1 N aqueous sodium hydroxide, and prehydrogenated. Freshly prepared catalyst consumed about 5 ml of hydrogen. (If no hydrogen is consumed in the prehydrogenation, the catalyst is no longer active.) A solution of the compound to be investigated (1 mmole) in ethanol (5 ml) was then added and hydrogenation carried out at room temperature and normal pressure (see above).

In the following the results of some of the hydrogenations listed in Tables 1–5 are briefly reported.

Hydrogenation of ethyl guaiacyl carbinol (III), ethyl guaiacyl carbinol methyl ether (XI) and 4-propioguaiacone (XXIV). One mmole of the compound and 0.2 g of PdCl₂-BaSO₄ catalyst were used in each experiment and the hydrogenation was carried out as described above. III and XI consumed 1 mmole, XXIV consumed 2 mmoles of hydrogen. When hydrogen consumption had ceased, the catalyst was removed by centrifuging, the solvent was evaporated and the residue dissolved in ether. The product obtained from the ethereal solution in each case was a light oil, which distilled at 0.3 mm Hg and 100° (bath temperature). The distilled oil (yield, about 80 %) was identified by refractive index (n_D^{20} , 1.5220) and comparison of infrared absorption spectra as 4-*n*-propylguaiacol (coerulignol).

Hydrogenation of ethyl veratryl carbinol (IV) and 4-propioveratrone (XXV) with PdCl₂-BaSO₄ in the same way yielded 4-*n*-propylveratrol¹⁹; n_D^{20} , 1.5175. (Found: OCH₃ 34.3. Calc. for C₁₁H₁₆O₂: OCH₃ 34.4.)

Hydrogenation of methylisoeugenolglycol- β -guaiacyl ether (IX) (0.5 mmole) with PdCl₂-BaSO₄ (0.5 g) for 24 h (see Fig. 1) gave a viscous oil, which distilled at 0.04 mm Hg and 210° (bath temperature). As expected for the *guaiacyl ether of veratrylpropanol-2*, the infrared spectrum of the product showed no hydroxyl absorption unlike the spectrum of IX which has a strong band at 3 500 cm⁻¹.

Hydrogenation of dihydro-dehydrodiisoeugenol methyl ether (XVI) (0.5 mmole) with PdCl₂-BaSO₄ (0.2 g) for 3 h (hydrogen consumption, 0.5 mmole) gave a viscous oil, which distilled at 0.04 mm Hg and 180° (bath temperature). (For 1-(3,4-dimethoxyphenyl)-2-(6-hydroxy-5-methoxy-3-propylphenyl)-propane a distillation temperature of about 218° at 1.5 mm Hg has been reported¹⁴.) The phenolic hydroxyl group liberated by the hydrogenolysis of XVI gives a band at 3 540 cm⁻¹ in the infrared spectrum of the reaction product.

Hydrogenation of dehydrodiconiferyl alcohol (XXI) (1 mmole) with PdCl₂-BaSO₄ (0.2 g) in the presence of anhydrous sodium acetate (0.03 g), for 5 min (1 mmole of H₂ consumed), gave dihydro-dehydrodiconiferyl alcohol (XVII), m.p. 120°, as reported by Freudenberg and Hübner¹⁵.

Hydrogenation of ethynyl veratryl carbinol (XLI)²⁰. A solution of XLI (2 mmole) in ethanol was added to a suspension of prehydrogenated nickel boride catalyst (about 0.2 g) in alkaline ethanol (see general procedure given above) and the mixture was stirred under hydrogen. The calculated amount of hydrogen (4 mmole, *i.e.*, 2 mole of H₂/mole) was consumed in about 1 h. The catalyst was removed by centrifugation and the solution was neutralised and then taken to dryness under reduced pressure. The residue on recrystallisation from ether-light petroleum gave colourless needles, m.p. 35°, identified by infrared absorption spectrum and mixed m.p. as *ethyl veratryl carbinol (IV)*. (This

substance, described by Roberti *et al.*²¹ as an oil, b.p. 102–103° at 0.2 mm, was previously obtained in this institute¹⁰ as a crystalline solid, m.p. 35–36°.)

On similar hydrogenation of *vinyl veratryl carbinol* (XL)²², 1 mole of hydrogen per mole was consumed with the production of IV.

Hydrogenation of coniferyl alcohol (XIX) with the nickel boride catalyst was complete after 20 min, 1 mole of hydrogen per mole being consumed. The oily reaction product crystallised from ether-light petroleum, after seeding with crystals of dihydroconiferyl alcohol (XLII)²³; m.p. and mixed m.p. 63°. This substance has been obtained previously as an oil, b.p. 196°/16 mm (Pearl¹⁷), and as a solid, m.p. 65° (Semetskina and Shorigina¹⁷).

Hydrogenation of veratrylacetone (XXXVI) with the nickel boride catalyst was complete after 80 min, 1 mole of hydrogen per mole being consumed. The oily reaction product crystallised from ether-light petroleum, yielding the previously unknown *1-(3,4-dimethoxyphenyl)-*n*-propan-2-ol* (XLIII) as needles, m.p. 40° (Found: C 67.07; H 8.11. Calc. for C₁₁H₁₆O₃: C 67.32; H 8.22.)

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