

Synthesis and Reactions of Hydroxylated Stilbenes and Their Possible Occurrence as Chromophore Precursor Structures in Lignin

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Chromophores which contribute to the color of kraft lignins and the generation of dihydroxystilbene structures as chromophore precursors are discussed briefly. The various *o,p'*- and *p,p'*-dihydroxystilbenes and 4,4'-dihydroxy-3,3'-dimethoxy-5-(4-hydroxy-3-methoxystyryl)stilbene, obtained via *Wittig* syntheses, are colorless substances which become more or less red colored when exposed to air. By reductive acetylation (zinc—acetic anhydride) stilbenoquinones, *o*- and *p*-quinonoid, diphenoquinoid, quinone methide, and stable oxygen radical structures are converted to colorless compounds, stabilized by simultaneous blocking of the formed phenolic hydroxyl groups. Application of that reaction to technical kraft lignin fractions let assume that a low number of chromophore structures (max. 5%) are responsible for the intensive color of the material.

Introduction

For many years the problem of color origin of kraft lignins seems to be a question of special interest to lignin chemists. The chemical nature of chromophores in kraft lignin is still unknown, but there exist valuable concepts for color formation¹⁻³. Stilbenes are discussed as chromophore precursors among various other leucochromophoric and chromophoric groups.

p,p'- and *o,p'*-Dihydroxystilbenes are formed under technical pulping conditions and are thought to be easily converted to chromo-

phores initiating thus color formation of lignin containing waste liquors and of residual lignin in pulps.

o,p'-Dihydroxystilbenes are generated from "phenylcoumaran" type units during kraft cooking as was shown by investigations of appropriate model compounds^{2, 4-6}. In accordance with these findings *Gierer et al.*⁷ isolated compounds with *o,p'*-dihydroxystilbene structure from kraft liquors. Acidolysis of "phenylcoumaran" structures may lead to the formation of this type of stilbenes as well, but only to a minor extent, the main route yields "phenylcoumarones"⁸.

Lundquist et al.^{9, 10} isolated after acidolytic treatment of spruce milled wood lignin among various other products 2,4'-dihydroxy-3,3'-dimethoxy-5-(3-hydroxy-2-propanone)- and 4,4'-dihydroxy-3,3'-dimethoxy-stilbene. The latter compound originates from 1,2-diaryl-propane-1,3-diol structures, which are converted to *p,p'*-dihydroxystilbenes in alkaline^{1, 11} as well as in acidic medium as was shown by use of model experiments. This reaction occurred during the acidolysis of spruce lignin according to *Adler et al.*⁸. 4,4'-Dihydroxy-3,3'-dimethoxystilbene was isolated from sulfite liquor¹², also on separation from various other reaction products formed during acidolysis of *Björkman* lignin⁹. It was obtained by alkaline treatment of various species of wood^{13, 14}, and its presence in kraft liquor¹⁵ and in kraft lignin³ was proved.

The configuration of the stilbenes formed during kraft cook of phenylcoumaran units or 1,2-diaryl-propane-1,3-diols was determined by means of spectroscopic methods^{1, 3, 6}. It was shown that the stilbenes possess *trans* configuration.

Worthy of note are the reaction possibilities of stilbenes. *o,p'*-Dihydroxystilbenes are partially oxidized to phenylcoumarones by oxygen in alkaline medium¹⁶ and are doubtlessly not strong potential chromophoric systems¹⁷, whereas oxidation of *p,p'*-dihydroxystilbenes results in the formation of the intensively colored *p,p'*-stilbenoquinones. With one electron transfer oxidants this reaction seems to proceed stepwise via the resonance stabilized semiquinonoid radical² which obviously represents an intensive color causing chromophore.

These colored oxidation products can be converted by a suitable reduction procedure to the corresponding colorless leuco compounds. Included in this paper is the conversion of *o*- and *p*-quinone, stilbenoquinone, quinone methide, and stable free radicals to uncolored products by means of a reductive acetylation method.

Results and Discussions

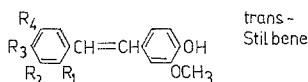
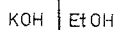
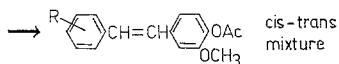
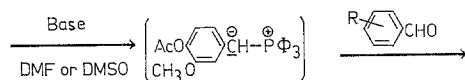
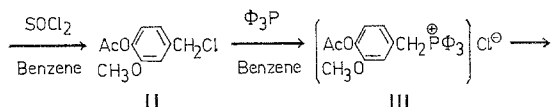
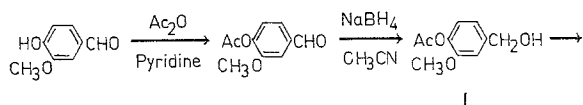
Syntheses of o,p'- and p,p'-dihydroxystilbenes

In general, stilbene syntheses are known from numerous publications^{18, 19}. Syntheses yielding unsymmetrical stilbene products carrying free phenolic hydroxyls in *o,p'*- and *p,p'*-positions are unknown,

however, with the exception of reports given by *Nelson* and *Wallis*¹⁷ and *Gierer et al.*¹⁸ at the Tappi Chromophore Symposium, held in Raleigh, N. C., 1972.

The synthetic method applied in this work, which was reported by us at the above mentioned meeting in 1972, has also been used by

General reaction scheme of stilbene syntheses



IV - VIII

IV: $\text{R}_1=\text{R}_2=\text{R}_4=\text{H}$; $\text{R}_3=\text{OH}$.

V: $\text{R}_1=\text{H}$; $\text{R}_2=\text{R}_4=\text{OCH}_3$;

$\text{R}_3=\text{OH}$.

VI: $\text{R}_1=\text{R}_2=\text{H}$; $\text{R}_3=\text{OH}$;

$\text{R}_4=\text{OCH}_3$.

VII: $\text{R}_1=\text{OH}$; $\text{R}_2=\text{OCH}_3$; $\text{R}_3=\text{R}_4=\text{H}$.

VIII: $\text{R}_1=\text{H}$; $\text{R}_2=4\text{-hydroxy-3-methoxy-}$

styryl; $\text{R}_3=\text{OH}$; $\text{R}_4=\text{OCH}_3$.

*Reimann*²⁰ who prepared natural occurring metasubstituted stilbenes, e.g. oxyresveratrol, piceatannol and rhapontigenin. *Reimann* used phosphonium salts with unprotected free hydroxyl groups which yielded the corresponding ylids by the action of strong bases.

In the case of ortho- and para-situated hydroxyl groups it was essential to protect the phenolic hydroxyls. Otherwise the formation of the phenolate anion would have prevented dehydrohalogenation and thus the formation of the ylid. Therefore, the phenolic aldehydes were acetylated by the acetic anhydride—pyridine method and consequently reduced to the acetoxybenzyl alcohol I with sodium borohydride in acetonitril. These compounds were converted to the acetoxybenzyl

halides **II** when treated with thionyl chloride in benzene solution. By a treatment with triphenylphosphine the corresponding acetoxybenzyl triphenylphosphonium salts **III** were obtained. The ylid formation was achieved by the action of a proton withdrawing base in *DMF* or *DMSO* as solvent. Finally, the acetylated aromatic aldehydes were added to perform the *Wittig* reaction yielding the acetylated stilbenes which were saponified afterwards (**IV—VIII**). (*Miller* and *Schuerch*²¹ tried an analogous synthesis, but not with promising results.)

The single conversions are summarized in the general reaction scheme. The experimental details are reported in the experimental section.

*Studies on Oxidation of Stilbenes and the Decoloration
of Oxidized Products by Means of Reductive Acetylation*

The *p,p'*- and *o,p'*-dihydroxystilbenes **IV—VII** synthesized by *Wittig* reaction are colorless substances. The same is true for the trihydroxy-styryl-stilbene **VIII** which does not have any *para*-conjugation.

Yet these colorless compounds become more or less red colored when exposed to air, even in solid state. The stilbenes are converted to stilbenoquinones and similar compounds²². The degree of oxidation depends on the nature of the substituents and on the surface area of the crystals. Investigations by means of *TLC* showed, that even intensively colored products have been oxidized only to a minor extent.

Reductive acetylations of oxidation products of stilbenes and other phenolic compounds were undertaken in order to study the problem of "color removal" from lignins. Independently from our work *Hayashi*²³ et al. investigated the effect of reductive acetylation on oxydiphenoquinones and soda lignin. The reductive acetylation with zinc in acetic anhydride allows the conversion of *o*- and *p*-quinones, diphenoquinones, quinone methides and stable oxygen radical structures to colorless compounds. The stilbene quinone chromophores are reduced to stilbenes by simultaneous stabilization of these structures against reoxidation by blocking the phenolic hydroxyl groups.

A comparison of the nmr-spectra and CH analytical data of acetylated (by sodium acetate—acetic anhydride) and reductively acetylated kraft lignin fractions shows the identical chemical composition of these lignin samples within the margin of error of the applied analytical methods, though the visible spectra differ remarkably. Thus, it can be estimated that at the utmost 5% of all the structural units are contributing to the intensive color of kraft lignins. (*Imsgard, Falkehag, and Kringstad*²⁴ determined the extent of *o*-quinonoid structures of spruce milled wood lignin to approximately 0.7%.)

Table 1. *Syntheses and Melting Points of Stilbenes and Their Acetates*

Reaction product	Starting material * (aldehyde component)	Method	Yield, %	Melting points, °C Stilbene	Melting points, °C Diacetate
4,4'-dihydroxy-3-methoxy- stilbene (IV)	p-hydroxybenzaldehyde	A	27-31	214-217	149-151
4,4'-dihydroxy-3,3',5-tri- methoxystilbene (V)	syringaldehyde	A	26 23-33	156-159	155-158
4,4'-dihydroxy-3,3'-dimethoxy- stilbene (VI)	vanillin	A	62	213-215	228-229
2,4'-dihydroxy-3,3'-dimethoxy- stilbene (VII)	o-vanillin	A	31	135-137	136-139
4,4'-dihydroxy-3,5'-dimethoxy- 3-(4-hydroxy-3-methoxystyryl)- stilbene (VIII)	,,5-formylvanillin [†]	B	30 10	183-186	196-200**

* Phosphonium chloride component in all cases: 4-acetoxy-3-methoxybenzyl-triphenylphosphonium chloride (III); aldehydes as acetates.

** Triacetate.

Table 2. Proton Chemical Shifts of Stilbenes (or Their Acetates)

Compound (solvent)	aromatic and olefinic H	CH ₃ O	δ-values (ppm) CH ₃ CO	ArOH
IV (acetone- <i>d</i> ₆) diacetate of IV (CDCl ₃)	6.73-7.60 (9 H) m	3.94 (3 H) s		8.38 (2 H) s
V (DMSO- <i>d</i> ₆)	7.00-7.70 (9 H) m	3.90 (3 H) s	2.35 (6 H) s	8.36 (1 H); 9.00 (1 H) s s
VI (acetone- <i>d</i> ₆) diacetate of VII	6.70-7.25 (7 H) m	3.90 (9 H) s		7.44 (2 H) s
triacetate of VIII (CDCl ₃)	6.70-7.30 (8 H) m	3.90 (6 H) s	2.32; 2.37 (6 H) d	
	6.78-7.24 (8 H) m	3.86; 3.90 (6 H) d	2.20; 2.50 (9 H) s	
	6.93-7.50 (12 H) m	3.93 (9 H) s		

Experimental

Melting points are uncorrected

Thin-layer Chromatography

The reaction products were investigated by *TLC* using silicagel HF₂₅₄₊₃₆₆ (E. Merck A.G., Darmstadt). As solvent systems benzene—glacial acetic acid—water (4:2:1; organic layer), benzene—ethyl acetate (4:1) or CHCl₃ were used.

Preparative Thin-layer Chromatography

Preparative *TLC* was performed using silicagel PF₂₅₄₊₃₆₆ (E. Merck A.G., Darmstadt). As solvent system benzene—glacial acetic acid—water (4:2:1; organic layer) was used. The stilbenes were extracted by CH₂Cl₂ from the silicagel under purified N₂.

Column Chromatography

Column chromatography was performed on silicagel 0.05–0.2 mm (E. Merck). CHCl₃ was used as solvent. The migration of stilbene products was followed by means of UV-irradiation (366 nm). Extended exposure towards UV-light has to be avoided on account of conversion of the stilbenes into red undefined products.

NMR Spectrometry

The nmr spectra were recorded on a Varian 60 Mc spectrometer using *TMS* as internal standard. The nmr-data are listed in Table 2.

Mass Spectrometry

The mass spectra were run on a Varian MAT-CH-7 spectrometer at 70 and 20 eV. The probe heater was kept at 80 and 100 °C. The spectral data are given on p. 693. The experimental CH-values of the synthesized stilbenes and their acetates were in full agreement with the calculated values.

Syntheses of Starting Materials

4-Acetoxy-3-methoxy-benzyl alcohol (**I**), a high viscous colorless oil, was prepared similarly to a method given in the literature²¹ by NaBH₄ reduction of vanillin acetate. Dry acetonitril was used as solvent. Yield 92% (*Mikawa*²⁵: 79%).

4-Acetoxy-3-methoxy-benzyl chloride (**II**). The conversion of the substituted benzyl alcohol to **II** was performed using an equimolar amount of SOCl₂ instead of excess as reported in literature²¹. Yield 94%, m. p. 44–45 °C (*Mikawa*: m. p. 46–47 °C) in contrary to the observation of *Miller* and *Schuerch*²¹ who did not succeed in crystallising the product.

4-Acetoxy-3-methoxy-benzyltriphenylphosphonium chloride (**III**). Compound **III** was obtained from reaction of equimolar amounts of the benzyl chloride **II** and triphenylphosphine as a white crystalline product (preparation similar to *Miller* and *Schuerch*²¹). Yield 85%, m. p. 235–237 °C (decomp.) (*Miller* and *Schuerch* reported 225 °C).

Picrate of III: Preparation according to a method given by *Wittig et al.*²⁶, m. p. (ethanol—water): 157–160 °C.

$C_{34}H_{28}N_3O_{10}P$. Calc. C 60.99, H 4.22, N 6.28, P 4.63.
Found C 61.09, H 4.18, N 6.33, P 4.67.

Acetylation of Phenolic Aldehydes

was carried out by applying conventional methods (pyridine, acetic anhydride).

Table 3. *Reductive Acetylation of Quinonoid Model Compounds*

Starting material	Isolated product
p-quinone	1,4-diacetoxy-benzene (m. p. 122 °C)
quinhydrone	1,4-diacetoxy-benzene (m. p. 122 °C)
4,6-di- <i>tert.</i> butyl-3-hydroxy- o-benzoquinone	colorless cryst. (m. p. 156–157 °C)
coerulignone	4,4'-diacetoxy-3,3',5,5'-tetramethoxy- 1,1'-biphenyl (m. p. 231–232 °C)
3,3'-dimethoxy-p-stilbenoquinone	4,4'-diacetoxy-3,3'-dimethoxystilbene (m. p. 228–229 °C)
2,3',5',6-tetra- <i>tert.</i> butyl- 4(4'-hydroxybenzylidene)-2,5- cyclohexadien-1-one	colorless crystals (m. p. 154–156 °C)

Syringaldehyde. The preparation was performed following the synthesis of 5-formylvanillin according to *Profft and Krause*²⁷. Thus, 60 g (0.39 mole) 2,6-dimethoxyphenol, 100 g (0.72 mole) hexamethylene tetramine, 170 ml glacial acetic acid, and 170 ml of water were refluxed for 2.5 hrs. 150 ml conc. HCl were added and boiling was continued for 10 mins. Then the mixture was poured onto crushed ice and allowed to stand over night. Filtration yielded 39.0 g (55%) raw syringaldehyde. The filtrate was extracted with NaHSO₃-solution, the extract washed with CHCl₃, filtered and acidified with 44 ml 50% H₂SO₄. The mixture was heated on a water bath and the formed SO₂ was expelled by bubbling air through the solution. 5.61 g product precipitated on cooling (i. e. 7.9%). The overall yield of purified aldehyde was more than 60% of the theoretical amount, m. p. 111–112 °C (from methanol—water 10 : 1).

Stilbene Syntheses

General Methods

Method A. A two-necked 250 ml round-bottomed flask is fitted with two pressure equalizing dropping funnels and gas inlet and outlet tube, thus allowing the protecting gas (N₂) to enter the apparatus via one dropping funnel and to leave it via the second.

10 mmoles (4.77 g) phosphonium salt **III** are placed in the flask and dissolved in 120 ml dry *DMF* under stirring. The apparatus is flushed for 0.5 hrs. with oxygen-free N₂, then as suspension of 11 mmoles (1.23 g) **K tert.** butylate in 60 ml dry *DMF* is added dropwise to the phosphonium salt.

The solution is stirred under N_2 for 6 hrs., then the solution of the aldehyde component (10 mmoles in 40 ml dry *DMF*) is added all at once. This mixture is stirred under N_2 for additional 12 hrs. Then the solvent is removed under vacuum at a bath temperature of 40 °C. To the oily residue a small amount of $NaHSO_3$ is added in order to prevent from oxidation by air. The reaction flask is then fitted with reflux condenser and dropping funnel. The latter contains a solution of 2.5 g KOH in 40 ml ethanol. The apparatus is flushed with N_2 for 0.5 hrs., then the ethanolic KOH is added dropwise to the oil. Saponification of the acetates is performed by refluxing the mixture for 15 mins. After cooling down to room temp. the solvent is removed under vacuum. The oily residue is dissolved under gentle warming in 300 ml of water and extracted with 3×70 ml benzene*. The phenolic products (stilbenes) are precipitated by passing CO_2 into the red aqueous alkaline solution. After reaching a $pH = 7$ the raw stilbene is isolated by filtration and dried over P_2O_5 in vacuum. The filtrate is extracted with 3×50 ml ether in order to separate from some by-products. Then the solution is acidified to $pH = 2$ with 1*N*-HCl. In most cases some stilbene precipitates on standing.

Method *B*. The apparatus used is the same as described for Method *A*. One dropping funnel contains 160 ml dry *DMF* (or 110 ml dry *DMSO*), the other is filled with the suspension of 11 mmoles (1.23 g) *K tert. butylate* in the same solvent. 10 mmoles (4.77 g) phosphonium salt **III** and 10 mmoles of the aldehyde component are introduced in solid state into the reaction flask and dissolved in *DMF* (or *DMSO*) under stirring, while nitrogen is passing through the apparatus. The solution of *K tert. butylate* is added dropwise over a period of 1.5 hrs. Stirring of the mixture under N_2 is continued over night. Work up as given under Method *A*.

Method *C*. The above described apparatus is also used for the following procedure. One dropping funnel contains the solution of 11 mmoles (1.36 g) 1,5-diaza-bicyclo[4.3.0]non-5-ene in 20 ml dry *DMF*, the other is filled with the solution of 10 mmoles of the aldehyde component in 40 ml *DMF*. 10 mmoles (4.77 g) phosphonium salt **III** are dissolved in 120 ml *DMF* under stirring and flushing with N_2 . After 0.5 hrs. the aldehyde is added all at once. Then the mixture is heated to 60–70 °C for 4 hrs. After cooling to room temp. the mixture is stirred over night. Work up as given in Method *A*.

Mass Spectra of Stilbenes (or Their Acetates)

The data listed here represent only a part of the respective mass spectra. Only fragments with a relative intensity ≥ 3 are considered here.

4,4'-Dihydroxy-3-methoxystilbene **IV**. m/e (I_{rel}): 243 (26); 242 (M^+ , 100); 227 (4); 211 (3); 210 (4); 209 (5); 199 (7); 198 (3); 181 (30); 171 (4); 170 (4); 169 (7); 165 (5); 157 (4); 153 (11); 152 (11); 151 (4); 128 (6); 127 (5); 121 ($M^{+}/2$; 2, 5); 115 (11).

4,4'-Diacetoxy-3,3',5-trimethoxystilbene (diacetate of **V**): 387 (4); 386 (M^+ , 16); 345 (8); 344 (30); 304 (5); 303 (20); 302 (100); 272 (5); 242 (3); 241 (3); 227 (3); 226 (3); 198 (3); 181 (3); 155 (3); 127 (3); 115 (4); 43 (20); metastable ions: m/e 307 and 265.

* The extract contains triphenylphosphine oxide and small amounts of triphenylphosphine.

4,4'-Dihydroxy-3,3'-dimethoxystilbene VI. 274 (4); 273 (18); 272 (M^+ , 100); 257 (1); 239 (2); 211 (10); 207 (5); 197 (6); 196 (4); 181 (4); 169 (6); 168 (5); 141 (3); 139 (3); 137 (19); 136 ($M^{++}/2$, 2, 4); 128 (3); 115 (4); 106 (4); 105 (3); 91 (6); 77 (5).

2,4'-Dihydroxy-3,3'-dimethoxystilbene VII. 274 (3); 273 (19); 272 (M^+ , 100); 271 (4); 257 (2); 243 (4); 239 (5); 229 (8); 225 (6); 213 (3); 211 (7); 207 (4); 197 (15); 196 (4); 181 (4); 169 (15); 168 (9); 149 (3); 141 (9); 139 (8); 131 (6); 129 (3); 128 (7); 127 (3); 115 (8); 77 (8).

2-Acetoxy-1,5-bis(4'-acetoxy-3'-methoxystyryl)-3-methoxybenzene (triacetate of VIII). 548 (3); 547 (9); 546 (M^+ , 25); 506 (3); 505 (14); 504 (42); 464 (3); 463 (17); 462 (57); 461 (8); 422 (6); 421 (27); 420 (100); 419 (8); 418 (3); 267 (5); 210 (10); 151 (11); 137 (8); 43 (86); metastable ions: m/e 465, 424, and 382.

General Procedure for Reductive Acetylation

0.2 g of the sample are mixed with 3 ml Ac_2O . To this solution (or suspension) a few crystals of sodium acetate are added and the whole mixture is refluxed for 2–3 mins. To the hot mixture an excessive amount of zinc dust is added, and heating is continued until the color has completely disappeared. After cooling to room temp., the excess of zinc dust is filtered and washed with acetic acid. The combined filtrates are poured onto crushed ice. Crystals are separating after the hydrolysis of the Ac_2O , isolated by filtration and dried. The remaining solution is carefully extracted with ether, the ether layer is washed with saturated $NaHCO_3$ -solution and finally with water. After drying over Na_2SO_4 the solvent is removed and the residue purified by distillation under vacuum.

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