

Acid Degradation of Lignin

V.* Degradation Products Related to the Phenylcoumaran Type of Structure

KNUT LUNDQUIST and KENNETH HEDLUND

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, Fack, S-402 20 Göteborg 5, Sweden

A preparation of lignin acidolysis products VII and VIII, starting from dehydrodiconiferyl alcohol (IX), is described.

Reinvestigation of the reaction product obtained on acidolysis of lignin model compound I revealed that, in addition to the previously obtained phenylcoumarone III, minor amounts of stilbene IV were formed. Final structural confirmation of product III was achieved by an independent synthesis.

On the basis of acidolysis experiments with lignin model compounds, primarily phenylcoumaran I, it is concluded that lignin acidolysis products VII and VIII originate from lignin structures of type X.

It has been found that dihydrodehydrodiconiferyl alcohol (I), a lignin model compound of the phenylcoumaran type, when heated in acid solution gives rise to the phenylcoumarone III.¹ The structure of compound III was derived from spectral and analytical data and the properties of two derivatives. Final structural confirmation of compound III has been achieved by an independent synthesis, described in the present paper (p. 2203).

Phenylcoumarone III has a strong, characteristic absorption in the UV region. This made it possible to obtain spectral evidence for the presence of the phenylcoumaran type of structure in spruce lignin by studying the spectral changes effected by heating in acid solution.¹ The acidic treatment preferred in these studies was refluxing with 0.2 M hydrogen chloride in dioxane : water (9 : 1).** On the basis of these investigations it was also possible to estimate the abundance of the phenylcoumaran type of structure. The results obtained indicated that structural elements of this type comprise about 20 % of the phenylpropane units of the lignin. Later, a compound

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** In the present paper, the term "acidolysis" is used specifically for this procedure.

of the phenylcoumarone type, *viz.* compound VII, was isolated from the reaction mixture obtained on 4 h acidolysis of spruce lignin;² the detection of this product in the lignin acidolysis mixture complements the above-mentioned spectral evidence for the presence of structural elements of the phenylcoumaran type in spruce lignin. It may be noted that in recent studies of the acidolysis mixture of a hardwood lignin (lignin from birch, *Betula verrucosa*), evidence for the presence of phenylcoumarone VII has been obtained.³

In connection with continued investigations of the low molecular weight products, formed on 4 h acidolysis of spruce lignin,^{4,5} more detailed knowledge concerning the reactions of the phenylcoumaran type of structure on acidolysis was desirable. The acidolysis of phenylcoumaran I was therefore subjected to further studies. It was found that the reaction mixture obtained on 4 h acidolysis of compound I contained, in addition to the earlier obtained phenylcoumarone III, minor amounts of stilbene IV. (This stilbene has previously been obtained in high yield on treatment of compound I under "kraft cooking" conditions.⁶) Stilbene IV is presumed to be formed, together with formaldehyde, by fragmentation of compound I *via* the benzylium ion II (Fig. 1). The finding

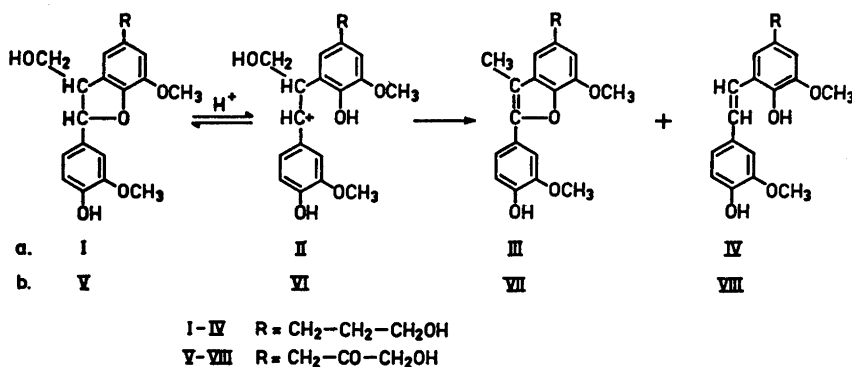


Fig. 1. a. Acidolysis of dihydrodehydrodiconiferyl alcohol (I). b. Acidolysis of ketol V, a postulated intermediate in the acidolysis of the reaction product, obtained on oxidation of dehydrodiconiferyl alcohol (IX) with perbenzoic acid.

that formaldehyde is obtained in about the same yield as stilbene IV supported this view.⁵ The formation of stilbene IV and formaldehyde from phenylcoumaran I can be regarded as a reversal of a Prins reaction. Similar reactions have been observed on acidolysis of other types of lignin model compounds.^{7,5} The formation of the main product, phenylcoumarone III, is also thought to proceed *via* the benzylium ion II.¹

In addition to the above-mentioned phenylcoumarone VII and a number of other products, stilbene VIII has been shown to be present among the low molecular weight phenols formed on 4 h acidolysis of spruce lignin.⁴ Structural proof of these two compounds as well as their preparation starting from dehydrodiconiferyl alcohol (IX), is described below. The acidolysis

experiments with model compound I suggest that the lignin acidolysis products VII and VIII originate from structural elements of the phenylcoumaran type. Ketol side chains of the type present in compounds VII and VIII arise on the acidolytic cleavage of arylglycerol- β -aryl ethers, such as XII.⁸ Compounds VII and VIII can therefore be considered to be formed from structural elements of the phenylcoumaran type, carrying a glycerol side chain which is linked to an adjacent unit by a β -ether bond, *i.e.* structural elements of type X (Fig. 2).

The formation, in the biosynthesis of lignin,⁹ of a sequence of guaiacylpropane units, as in structure X, should involve an oxidative coupling of coniferyl alcohol (XI) with a phenolic unit included in a guaiacylglycerol- β -

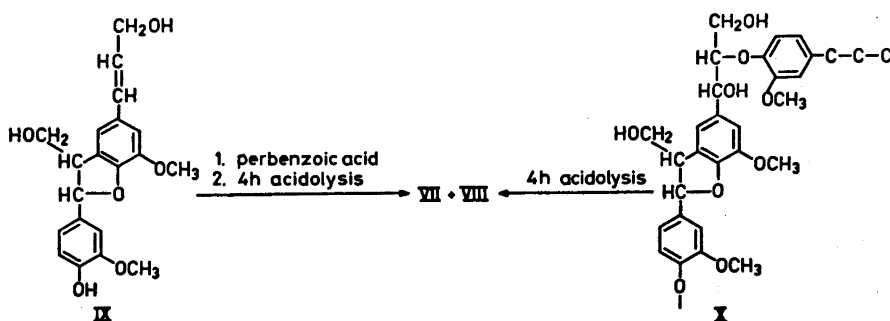


Fig. 2. Preparation of lignin acidolysis products VII and VIII (considered to originate from lignin structures of type X), starting from dehydrodiconiferyl alcohol (IX).

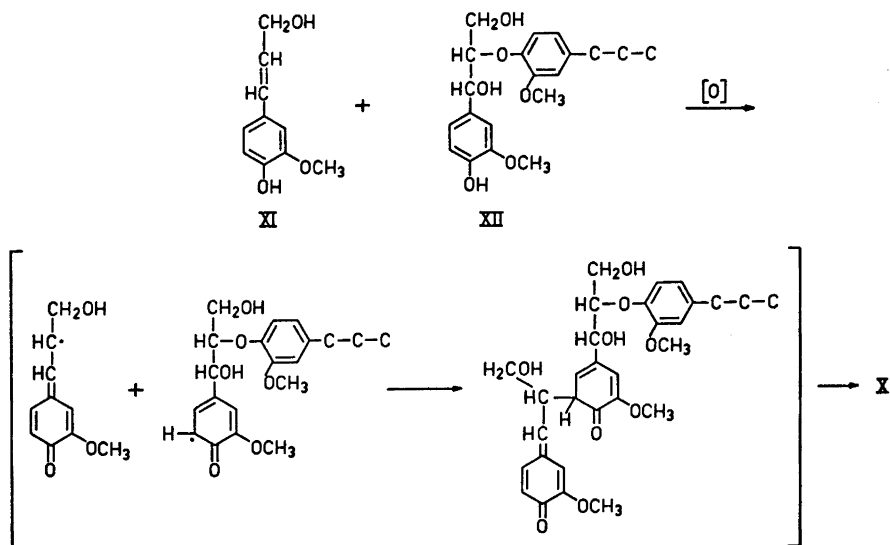


Fig. 3. Formation of structural elements of type X in the biosynthesis of lignin.

aryl ether structure (XII) (Fig. 3). The reaction shown in Fig. 3 exemplifies the growth of the lignin molecule by oxidative coupling of coniferyl alcohol and a phenolic end group. A second reaction route for the introduction of coniferyl alcohol proceeds *via* an oxidative dimerization;⁹ the fact that the dimers IX, guaiacylglycerol- β -coniferyl ether, and d,1-pinoresinol are obtained on mild hydrolysis of spruce wood¹⁰ provides evidence for the participation of this reaction in lignin formation. Interestingly, reaction mixtures obtained on oxidation of coniferyl alcohol *in vitro* have been shown to contain oligomeric products, the structures of which indicate that both the above-mentioned reactions have been involved in their formation.⁹

According to the generally accepted view for the formation of lignin,⁹ the occurrence of oxidative dimerization of coniferyl alcohol is a necessary condition for the formation of pinoresinol structures accessible to acidolytic liberation of pinoresinol (*e.g.* pinoresinol molecules linked to the lignin merely by β -ether bonds). The number of such pinoresinol structures in spruce lignin seems to be very small; in recent studies of the reaction mixture obtained on 4 h acidolysis of spruce lignin pinoresinol could not be detected, and separate experiments were made which showed that the amount which could have been formed (including epipinoresinol) was considerably < 0.1% of the lignin.⁴ Because the pinoresinol type of structure seems to be relatively abundant (according to a recent estimation,¹¹ 5–10% of the units in soft wood lignin are present in such structures), this finding suggests that the proportion of the pinoresinol type of units which gives rise to pinoresinol on acidolysis must be small, and can therefore be interpreted to indicate that oxidative dimerization of coniferyl alcohol participates only to a small extent in lignin formation.

In studies with spruce lignin, it has been found that the number of coniferyl alcohol end groups is rather small.¹² This fact similarly suggests that oxidative dimerization of coniferyl alcohol only plays a limited role in lignin formation, since the more prominent dimers obtained on oxidation of coniferyl alcohol *in vitro*⁹ include IX and guaiacylglycerol- β -coniferyl ether, which contain coniferyl alcohol units with etherified phenolic group.

Preparation of phenylcoumarone VII and stilbene VIII

Phenylcoumarone VII and stilbene VIII were prepared from dehydrodiconiferyl alcohol¹³ (IX). Treatment of compound IX with perbenzoic acid (or monophrthalic acid), followed by 4 h acidolysis, resulted in the formation of phenylcoumarone VII and minor amounts of stilbene VIII (Fig. 2). It is assumed that the peracid oxidizes the double bond in compound IX to give an epoxide. The structure of the oxidation product, however, has not been proved.

The formation of compounds VII and VIII from compound IX involves conversion of an allyl alcoholic side chain into a ketol side chain. To study this particular step in the reactions leading to compounds VII and VIII, 3-(3,4-dimethoxyphenyl)-2-propene-1-ol (XIII) was used as a model compound. It was found that compound XIII on oxidation with perbenzoic acid, followed

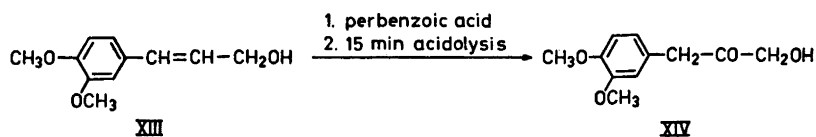


Fig. 4. Preparation of ketol XIV from 3-(3,4-dimethoxyphenyl)-2-propene-1-ol (XIII).

by brief acidolysis, gave ketol XIV (Fig. 4). This result and the fact that the phenylcoumaran-phenylcoumarone conversion seems to be a relatively slow reaction¹ suggest that at an early stage of the acidolysis of the oxidation product formed from compound IX, ketol V is present in the acidolysis mixture. The formation of compounds VII and VIII from the postulated intermediate ketol V (*via* benzylum ion VI) on prolonged acidolysis is quite analogous to the formation of compounds III and IV on acidolysis of compound I (Fig. 1).

The synthesis, spectral data, and determination of the elemental compositions by mass measurements of the molecular ions established the structures of the lignin acidolysis products VII and VIII.

Synthesis of phenylcoumarone III*

Phenylcoumarone III was prepared from dehydrodiisoeugenol^{14,15} (XV) in a four step synthesis (Fig. 5). The propenyl side chain of XV has been shown to have the *trans*-configuration.¹⁵ A stereoisomer of XV, which differs from XV only in having the *cis*-configuration in the propenyl side chain, has recently been prepared.¹⁶

In the first step, the methyl group in the propenyl side chain was oxidized to a formyl group with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), accord-

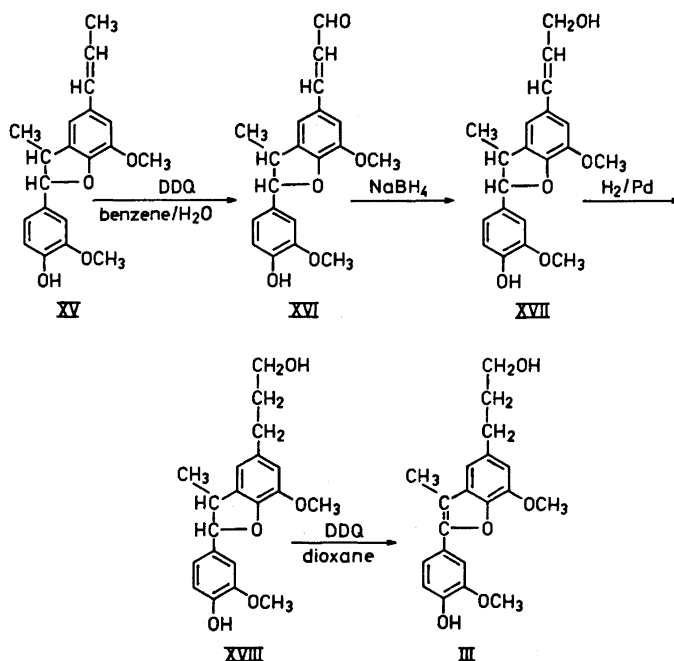
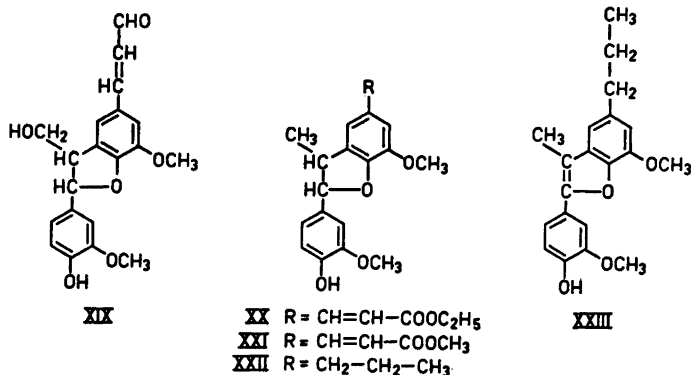


Fig. 5. Synthesis of phenylcoumarone III, starting from dehydrodiisoeugenol (XV).

* Presented at Det 13. Nordiske Kemikermøde, Copenhagen, August 19–23, 1968.

ing to a method for the conversion of arylpropenes into cinnamaldehydes with this oxidant reported by Adler and co-workers.¹⁷ Benzene, containing water, was used as solvent (the reaction requires the presence of water^{17c}). Aldehyde XVI (m.p. 110–112°) was obtained in good yield. Spectral and analytical data provided structural proof for compound XVI. Additional support for the structure of aldehyde XVI was obtained by comparing its spectral properties with those of a related compound, "Substanz E" (XIX), which has been described by Freudenberg and Lehmann.¹⁸ We prepared "Substanz E" by the oxidation of compound IX with DDQ (for the use of DDQ in the preparation of unsaturated carbonyl compounds from allylic alcohols, see Ref. 19). "Substanz E" and compound XVI gave both a positive "Wiesner reaction" (see Ref. 20), *i.e.* an intense violet colour appeared on treatment with phloroglucinol-hydrochloric acid.

In preliminary experiments, when commercial methylene chloride was used as solvent in the preparation of aldehyde XVI, an additional product was obtained which was shown to be ethyl ester XX (m.p. 173–175°); the ethyl group originated from ethanol, present in the solvent. Thus, in experiments with benzene : ethanol (19 : 1) as solvent, ester XX was the major product. With benzene : methanol (19 : 1) as solvent, the methyl ester XXI (m.p. 186–187°) was obtained. The structures of compounds XX and XXI were derived from spectral and analytical data. The NMR spectra of both esters showed a *J* value of 16 Hz for the coupling between the olefinic protons; this indicates that the compounds have the *trans*-configuration in the unsaturated side chain.²¹ In the case of compound XXI it was shown that 1 mol of CH₃OH per mol XXI was liberated on saponification; this provides additional support for the presence of a methyl ester group in XXI. On treatment with DDQ in benzene : ethanol (19 : 1), aldehyde XVI remained essentially unchanged. This indicates that the formation of esters from XV does not proceed to any appreciable extent *via* the aldehyde XVI.



Aldehyde XVI was reduced to alcohol XVII (m.p. 113–115°) with sodium borohydride. In the case of compound XVI, as well as compound XVII, the NMR spectrum showed a *J* value for the coupling between the olefinic protons of 16 Hz; this indicates that these compounds have the *trans*-configuration in the unsaturated side chain.²¹ Catalytic hydrogenation of alcohol XVII gave alcohol XVIII (m.p. 84–86°). As catalyst, 5 % Pd/BaSO₄

was used. In preliminary experiments with 10 % Pd/C as catalyst, the formation of compound XXII²² was a relatively important side reaction.

In the final step, the phenylcoumaran XVIII was dehydrogenated with DDQ in dioxane solution to give the desired phenylcoumarone III. Dehydrogenation of dihydrodehydrodiisoeugenol (XXII) with the same oxidant gives phenylcoumarone XXIII,^{17b,16} previously obtained by heating XXII with sulphur.²³ Synthetic III was found to be identical with the product obtained by acidolysis of compound I by IR and mixed m.p.

All the reaction steps in the synthesis of phenylcoumarone III involve changes in the conjugated system. The reactions are therefore accompanied by considerable changes of the UV properties (UV spectra of compounds XVI, XVII, XVIII, and III are given in Fig. 6; the UV spectrum of compound XV, which resembles that of compound XVII, is given in Ref. 24).

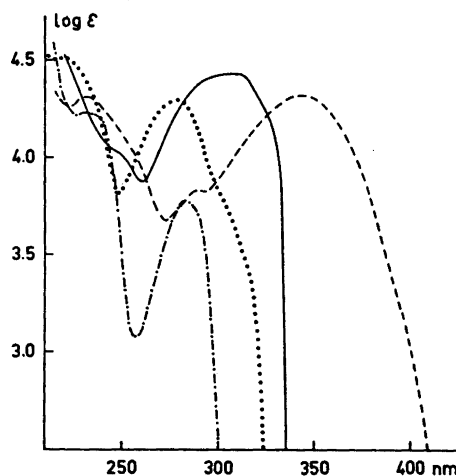


Fig. 6. UV spectra of compounds XVI (---), XVII (···), XVIII (-·-·), and III (—).

EXPERIMENTAL

Materials. Dioxane and ethyl acetate were purified according to Ref. 25. Silica gel for column chromatography was Mallinckrodt analytical reagent, 100 mesh, dried at 110° overnight. The 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) used was commercial grade. Dehydrodiisoeugenol (XV) was prepared according to the procedure described by Leopold.²⁶

UV spectra were recorded on a Beckman DK 2A instrument. Unless otherwise stated, abs. ethanol was used as a solvent. **IR spectra** were recorded on a Beckman IR-9 instrument, using KBr pellets. **NMR spectra** were recorded on a Varian A-60 instrument with TMS as internal standard. **Mass spectra** were taken on an AEI model MS 902 instrument. This equipment was also used for mass measurements; the results obtained were within 1 ppm of the calculated values.

Thin layer chromatography was carried out on plates coated with a 0.3 mm thick layer of silica gel (Merck HF₂₅₄). As eluting agents, benzene : ethyl acetate (1 : 1) (R_F values: VIII, 0.18; IV, 0.22; XIV, 0.24; VII, 0.25; III, 0.28; XVIII, 0.28; XXIII, 0.52) and benzene : ethyl acetate (4 : 1) (R_F values: XVI, 0.28; XXI, 0.39; XX, 0.41) were used. Spots were made visible by exposure to iodine vapour. In general, guaiacol com-

pounds appear as light brown spots on this treatment. Spots of phenylcoumarones III, VII, and XXIII acquired a green colour which, however, slowly turned to light brown. Stilbenes IV and VIII appeared as dark brown spots.

Preparative thin layer chromatography was performed on plates similar to those used for analytical purposes and with benzene : ethyl acetate (1 : 1) as eluting agent. The zones of silica gel containing the materials of interest, detected by UV light, were scratched off and the compounds eluted with acetone.

Acidolysis of dihydrodehydrodiconiferyl alcohol (I). A solution of 50 mg dihydrodehydrodiconiferyl alcohol¹³ (I) in 10 ml 0.2 M HCl in dioxane : water (9 : 1) was refluxed for 4 h (nitrogen atmosphere). Four and a half ml of 0.4 M NaHCO₃ were added to the cooled reaction mixture, which then was extracted with 3 × 10 ml of chloroform. The extract was dried over anhydrous Na₂SO₄, and the solvent was removed by film evaporation. A partly crystalline residue was obtained. Soaking with 2 × 0.5 ml of benzene : ethyl acetate (1 : 1) left a crystalline residue, which was identified as phenylcoumarone III.¹ As indicated by thin layer chromatography, compounds III and IV were present in that portion of the reaction mixture which dissolved in benzene : ethyl acetate (1 : 1). Separation of stilbene IV was accomplished by chromatography on a silica gel column with benzene : ethyl acetate (1 : 1) as eluting agent, followed by preparative thin layer chromatography. An oil weighing 4.4 mg was obtained. Inoculation with stilbene IV gave crystals of m.p. 112°. The product was identified as stilbene IV (m.p. 113.5–114°⁶) by IR and mixed m.p.

Syntheses

Preparation of phenylcoumarone VII and stilbene VIII. To a solution of 0.30 g (0.84 mmol) of dehydrodiconiferyl alcohol¹³ (IX) (preparation, see Refs. 27 and 1) in 100 ml of chloroform, 0.13 g (0.94 mmol) of perbenzoic acid in 24 ml of chloroform was added. The consumption of perbenzoic acid was followed by titrating samples of the reaction mixture, according to Ref. 28. After 20 h at room temperature, when 0.80 mmol of perbenzoic acid had been consumed, the reaction mixture was shaken once with 0.4 M NaHCO₃ and dried over anhydrous Na₂SO₄. The solvent was removed by film evaporation. The oily residue was refluxed with 0.2 M HCl in dioxane : water (9 : 1) for 4 h (nitrogen atmosphere). After being cooled, the reaction mixture was neutralized with 0.4 M NaHCO₃ and extracted with chloroform. The obtained extract was dried over anhydrous Na₂SO₄, and the solvent was removed by film evaporation. From the reaction product, fractions of phenylcoumarone VII and stilbene VIII, weighing 59 and 10 mg, respectively, could be separated. Separation was accomplished by gel filtration and chromatography on a silica gel column, according to the procedures described for the separation of the same products from the reaction mixture obtained on 4 h acidolysis of spruce lignin.⁴ Similar results have been obtained in experiments with monophtalic acid as oxidant.

Phenylcoumarone VII was obtained as crystals (m.p. 110°) from methylene chloride/petroleum ether or ethyl acetate/hexane. From benzene, a crystalline product with an unsharp m.p. (60–90°) was obtained. The NMR spectrum indicated that the latter product contained 1 mol of benzene per mol of compound VII. The UV spectrum of compound VII (λ_{\max} 308 nm, ϵ 25 000) was very similar to that of compound III. NMR spectrum (δ values, solvent : acetone-*d*₆): 2.41, singlet (3H, CH₃-C); 2.9, singlet (1H, alc.-OH); 3.87, singlet (2H, C-CH₂-C); 3.95, singlet (3H, CH₃-O); 4.00, singlet (3H, CH₃-O); 4.32, singlet (2H, C-CH₂-O); \approx 7.0, multiplet (5H, aromatic protons); 7.9, singlet (1H, phenolic-OH). Signals assigned to protons in the methyl groups had the same δ -values in the NMR spectra of compounds VII and III. The IR spectrum showed a band at 1720 cm⁻¹ (unconjugated carbonyl). A prominent peak in the mass spectrum was the molecular ion (*m/e* 356). By mass measurements of the molecular ion, the elemental composition was determined as C₂₀H₂₀O₆, which is in accord with structure VII.

Stilbene VIII was purified by preparative thin layer chromatography, and crystallized from methylene chloride. A product with m.p. 169–172° was obtained. The UV spectrum showed a maximum at 326 nm. In alkaline solution (0.1 M NaOH) the maximum was shifted to 376 nm. In both cases, ϵ_{\max} was of the order 20 000 (the amount of stilbene

VIII available did not permit more precise determinations). The UV properties are very similar to those of stilbene IV (see Ref. 6). The IR spectrum showed a band at 1725 cm^{-1} (unconjugated carbonyl). The mass spectrum showed a molecular ion at m/e 344. Mass measurements showed that the molecular ion had the elemental composition $\text{C}_{18}\text{H}_{20}\text{O}_6$, which is in accord with structure VIII.

Preparation of 1-hydroxy-3-(3,4-dimethoxyphenyl)-2-propanone (XIV) from compound XIII. Compound XIII²⁹ was oxidized with perbenzoic acid and subjected to acidolysis as described above with compound IX, but the acidolysis was carried out for 15 min only. From the reaction mixture, ketol XIV could be separated in moderate yield by chromatography on a silica gel column with benzene : ethyl acetate (1 : 1) as eluting agent. The product was identified with a synthetic sample³⁰ by IR and thin layer chromatography.

“Substanz E” (XIX). Solutions of 0.10 g (0.28 mmol) of dehydrodiconiferyl alcohol (IX) (preparation, see Refs. 27 and 1) and 0.10 g (0.44 mmol) of DDQ in methylene chloride were mixed (total amount of solvent 75 ml). After 1 h, the reaction mixture was shaken with a solution of 0.44 mmol of ascorbic acid in 25 ml of water, to reduce excess DDQ to the corresponding hydroquinone, and then washed by shaking with a small amount of water. The reaction mixture was dried over anhydrous Na_2SO_4 , and the solvent was removed by film evaporation. The obtained residue was dissolved in a small amount of methylene chloride, and a few drops of petroleum ether were added. The solution was allowed to stand one day in a refrigerator, whereupon 42 mg of pale yellow crystals, m.p. 156° , precipitated. The IR spectrum of the product was identical with that given for “Substanz E”¹⁸ (XIX) (m.p. $156-157^\circ$ ¹⁸).

Aldehyde XVI. Solutions of 0.65 g (2 mmol) of dehydrodiisoeugenol (XV) and 1.14 g (5 mmol) of DDQ in benzene containing water* were mixed (total amount of solvent 100 ml). After 1 h, the reaction mixture was shaken with 5 mmol of ascorbic acid in 50 ml of water, to reduce excess DDQ to the corresponding hydroquinone, and was then washed by shaking with 50 ml of water. The reaction mixture was dried over anhydrous Na_2SO_4 , and the solvent was removed by film evaporation. The residual oil crystallized on addition of a few drops of ethanol. The product (0.49 g) melted unsharply at 100° . Purification was accomplished by chromatography on a silica gel column ($2 \times 12\text{ cm}$; 20 g SiO_2), using benzene : ethyl acetate (4 : 1) as eluting agent. From the column, 0.43 g of a product with m.p. $109-111^\circ$ was obtained. Recrystallization from ethanol gave 0.31 g of XVI (yield 46 %), m.p. $110-112^\circ$. (Found: C 70.28; H 6.00; O 23.37; OCH_3 18.03. Calc. for $\text{C}_{18}\text{H}_{14}\text{O}_3$ (OCH_3)₂: C 70.58; H 5.92; O 23.50; OCH_3 18.24.) The IR spectrum showed a strong band at 1670 cm^{-1} ($\text{C}=\text{O}$). The UV spectrum (Fig. 6) showed maxima at 230 nm ($\log \epsilon$ 4.31), 288–289 nm ($\log \epsilon$ 3.83), and 343 nm ($\log \epsilon$ 4.32). NMR spectrum (δ units, solvent: chloroform-*d*): 1.41 (3H, doublet, $J = 6.7\text{ Hz}$; CH_3-C),

3.5 (1H, multiplet; $\text{C}-\text{CH} \begin{array}{l} \diagup \text{C} \\ \diagdown \text{C} \end{array}$), 3.86 (3H, singlet; $\text{O}-\text{CH}_3$), 3.92 (3H, singlet; $\text{O}-\text{CH}_3$),

5.20 (1H, doublet, $J = 9\text{ Hz}$; $\text{O}-\text{CH} \begin{array}{l} \diagup \text{C} \\ \diagdown \text{C} \end{array}$), 6.60 (1H, doublet of doublets, $J = 16\text{ Hz}$, $J = 7.5$

Hz; $\text{C}=\text{CH}-\text{CO}-$), 5.89 (1H, singlet; $-\text{OH}$), ≈ 6.9 (5H, multiplet; aromatic protons), 7.46 (1H, doublet, $J = 16\text{ Hz}$; $\text{C}-\text{CH}=\text{C}-\text{CO}-$), 9.64 (1H, doublet, $J = 7.5\text{ Hz}$; $-\text{CHO}$).

Ethyl ester XX. To a solution of 0.33 g (1 mmol) of dehydrodiisoeugenol (XV) in a mixture of 70 ml of benzene and 5 ml of ethanol, a solution of 0.68 g (3 mmol) of DDQ in 25 ml of benzene was added. After 1 h, the reaction mixture was shaken with a solution of 3 mmol of ascorbic acid in 25 ml of water, to reduce excess DDQ to the corresponding hydroquinone, and was then washed by shaking with 25 ml of water. The reaction mixture was dried over anhydrous Na_2SO_4 , and the solvent was removed by film evaporation. A residue weighing 0.31 g was obtained. Ester XX was separated by chromatography on a silica gel column ($2 \times 37\text{ cm}$; 60 g SiO_2) with benzene : ethyl acetate (4 : 1) as eluting agent. Crystals (0.20 g) with m.p. $163-171^\circ$ were obtained. (A fraction weighing 50 mg, consisting essentially of aldehyde XVI, was eluted after ester XX.) Recrystalliza-

* Benzene was shaken with water in a separatory funnel for a few minutes, and the benzene layer separated the following day; the solubility of water in benzene at 20° is 0.06.³¹

tion from methylene chloride/hexane gave 135 mg of XX (yield 35 %), m.p. 173–175°. (Found: C 68.30; H 6.15. Calc. for $C_{21}H_{24}O_6$: C 68.74; H 6.29.) Alkoxy (Zeisel): found 2.96 mol/mol; calc. for structure XX, 3 mol/mol (2 OCH_3 and 1 OC_2H_5). The IR spectrum showed a band at 1700 cm^{-1} ($C=O$). The UV spectrum showed maxima at 223 nm ($\log \epsilon$ 4.35) and 327 nm ($\log \epsilon$ 4.28). NMR spectrum (δ units, solvent: chloroform-*d*): 1.34 (3H,

triplet, $J=7.0$ Hz; CH_3-C-O), 1.40 (3H, doublet, $J=7.1$ Hz; CH_3-C), 3.5 (1H,

multiplet; $C-CH$), 3.86 (3H, singlet; $O-CH_3$), 3.90 (3H, singlet; $O-CH_3$), 4.27

(2H, quartet, $J=7.1$ Hz; $C-CH_2-O$), 5.17 (1H, doublet; $J=9$ Hz; $O-CH$), 6.31

(1H, doublet; $J=16$ Hz; $C=CH-CO-$), ≈ 6.9 (5H, multiplet; aromatic protons), 7.67 (1H, doublet; $J=16$ Hz; $C-CH=C-CO$).

Methyl ester XXI. Compound XV (0.33 g, 1 mmol) was treated with DDQ as described above in the preparation of ethyl ester XX, but with methanol instead of ethanol present in the reaction mixture. From the crude product (0.31 g), the major component was separated by chromatography on a silica gel column, using benzene : ethyl acetate (4 : 1) as eluting agent. A crystalline product (0.17 g) with m.p. 182–185° was obtained. Recrystallization from methylene chloride/hexane gave 0.12 g of XXI (yield 32 %), m.p. 186–187°. (Found: OCH_3 24.91. Calc. for structure XXI: OCH_3 25.14.) The IR spectrum showed a strong band at 1710 cm^{-1} ($C=O$). The UV spectrum showed a maximum at 327 nm ($\log \epsilon$ 4.29). The NMR spectrum agreed with that of compound XX with the exception of an additional signal at $\delta=3.80$ (3H, singlet), assigned to the protons in the methyl ester group, and the absence of the signals due to the protons in the ethyl group. On saponification (heating with excess 0.1 NaOH in dioxane : water (1 : 1) at 100° for 1 h), 1 mol of CH_3OH (determined by gas chromatography) per mol XXI was obtained; this is in accord with the presence of a methyl ester group in XXI.

Alcohol XVII. To a solution of 0.34 g aldehyde XVI in 10 ml of methanol, 0.34 g of $NaBH_4$ dissolved in 10 ml 0.04 M NaOH was added. After 1 h, the reaction mixture was acidified to pH 4 with dilute hydrochloric acid, and extracted with a total of 50 ml of chloroform. The extract was dried over anhydrous Na_2SO_4 , and the solvent was removed by film evaporation. A crystalline residue (m.p. 95–113°), weighing 0.30 g, was obtained. Recrystallization from ethyl acetate/hexane gave 0.20 g of XVII (yield 58 %), m.p. 113–115°. (Found: C 69.89; H 6.52; OCH_3 17.72. Calc. for $C_{18}H_{18}O_3(OCH_3)_2$: C 70.16, H 6.48; OCH_3 18.13.) The UV spectrum (Fig. 6) showed a maximum at 278 nm ($\log \epsilon$ 4.30). Signals due to protons in the allyl alcoholic side chain appeared in the NMR spectrum (a Varian HA-100 instrument was used, solvent: chloroform-*d*) at $\delta=4.30$ (2H, doublet, $J=5$ Hz; $C-CH_2-O$), $\delta=6.23$ (1H, doublet of triplets, $J=16$ Hz, $J=5$ Hz; $C=CH-C-O$), and $\delta=6.59$ (1H, doublet, $J=16$ Hz; $C-CH=C-C$). On irradiation of the peak at $\delta=4.30$ the peak at $\delta=6.23$ appeared as a doublet ($J=16$ Hz).

Alcohol XVIII. Alcohol XVII (0.20 g) was hydrogenated in 30 ml of ethanol, using 0.20 g 5 % Pd/ $BaSO_4$ (Fluka) as catalyst. After 7 min, when the calculated amount of hydrogen had been consumed, the hydrogenation was interrupted. The catalyst was filtered off, and the solvent was removed by film evaporation. A crystalline residue (0.19 g), melting at about 64°, was obtained. Purification was accomplished by chromatography on a silica gel column, using benzene : ethyl acetate (1 : 1) as eluting agent. From the column, 0.17 g of XVIII (85 % yield), m.p. 84–86°, was obtained. (On recrystallization from ethanol or methylene chloride/hexane products of lower m.p. were obtained. However, on storage in vacuum in a desiccator, the m.p. changed to 84–86°.) (Found: C 69.73; H 7.15; OCH_3 18.04. Calc. for $C_{18}H_{18}O_3(OCH_3)_2$: C 69.75; H 7.02; OCH_3 18.02.) The UV spectrum (Fig. 6) showed maxima at 233 nm ($\log \epsilon$ 4.23) and 282 nm ($\log \epsilon$ 3.79).

Phenylcoumarone III. Solutions of 0.29 g (0.84 mmol) of alcohol XVIII and 0.58 g of DDQ (2.6 mmol) in dioxane were mixed (total amount of solvent, 20 ml). After 1 h, 25 ml of chloroform was added to the reaction mixture, which was subsequently shaken with a solution of 2.6 mmol of ascorbic acid in 25 ml of water, to reduce excess DDQ

to the corresponding hydroquinone. The organic layer was then dried over anhydrous Na_2SO_4 , and the solvent was removed by film evaporation. A brown oil, weighing 0.28 g, was obtained. The presence of phenylcoumarone III in the product was indicated by thin layer chromatography. Separation of compound III was accomplished by chromatography on a silica gel column (2×20 cm; 30 g SiO_2), using benzene : ethyl acetate (1 : 1) as eluting agent. Those effluent fractions, which according to thin layer chromatography contained phenylcoumarone III, were collected, and the solvent was evaporated. A crystalline residue (0.10 g) with m.p. $160-170^\circ$ was obtained. Recrystallization from 2-3 ml of methanol gave 42 mg of crystals, melting at $170-172^\circ$. By IR and mixed m.p., the product was shown to be identical with the phenylcoumarone III (m.p. 173°), obtained by acidolysis of compound I. The UV spectrum (Fig. 6) showed a maximum at 308 nm ($\log \epsilon$ 4.44).

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