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The Reactions of Lignin During Sulphate Pulping

Part XII.* Reactions of Intermediary *o,p'*-Dihydroxy-stilbene Structures

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The transformations of phenylcoumaran structures in lignin during alkali- and sulphate pulping have been further studied using dihydro-dehydro-diisoeugenol as a model. The primary reaction product, an *o,p'*-dihydroxy-stilbene, is partly oxidised to a phenylcoumarone by the oxygen present in the alkaline pulping liquors. A small part of the stilbene undergoes cleavage of the α-aryl, α'-aryl, and α,α'-C–C-linkages. Plausible paths for the formation of these secondary reaction products are outlined in Schemes 1 and 2.

Phenylcoumaran structures constitute one of the major structural elements in lignin.[2–4] In previous communications in this series it has been shown that treatment of a phenolic model (I), representing these structures, with either sodium hydroxide [5] or white liquor [6]*** under pulping conditions, but with replacement of air by nitrogen, produces an *o,p'*-dihydroxy-stilbene (II) (*cf.* also Ref. 7). This has been isolated and purified as the diacetate.[5] It has been proposed that this structural change involves an alkali-promoted cleavage of the dihydrofurane ring with the formation of a methylene quinone intermediate, followed by the elimination of the β-proton to yield the stable stilbene system.[5]

The conversion phenylcoumaran → stilbene, brought about by alkali, undoubtedly constitutes the primary process. However, there is also a series of secondary reactions taking place to varying extents. These are the subject of the present paper.

Dihydro-dehydro-diisoeugenol (I) was treated with 2 N sodium hydroxide or with white liquor at 180° for 3 h in the presence of air. The resulting phenolic

* Part XI, see Ref. 1.

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*** The term "white liquor" refers to a solution of NaOH (3.5 g) $Na_2S.9H_2O$ (3.1 g) in water (100 ml).

products were separated as acetates by preparative column and gas liquid chromatography. The structures of the acetates were assigned on the basis of their analyses, NMR- and/or mass spectra.

RESULTS AND DISCUSSION

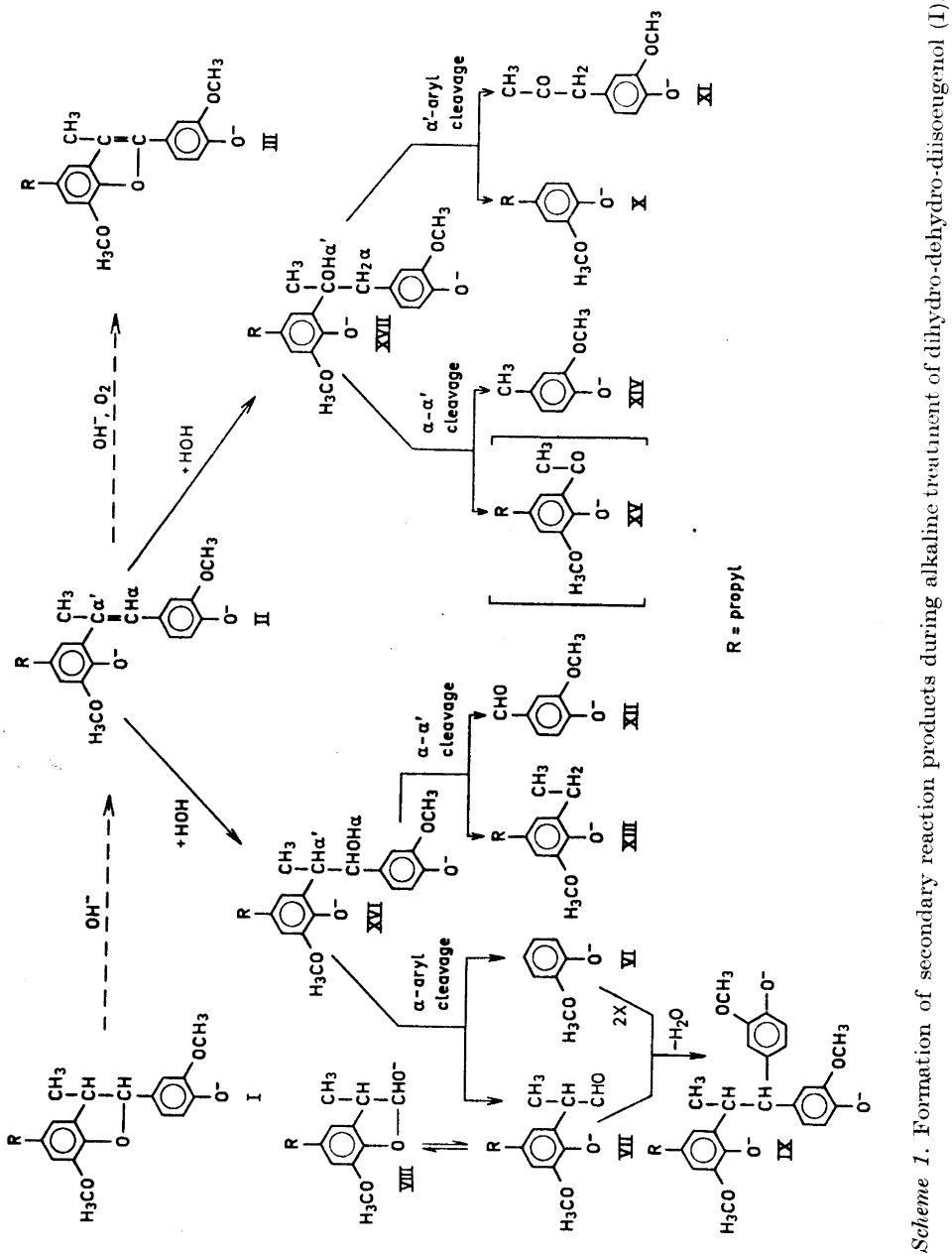
In Scheme 1 the products identified are summarised and plausible routes for their formation are suggested. The outline presumes the *o,p'*-dihydroxy-stilbene II, characterised in this work as the *cis*- and *trans*-forms of the di-acetates, to be the common intermediate in the formation of the other products. This assumption is supported by the fact that treatment of stilbene II with 2 N sodium hydroxide or with white liquor at 180° without the exclusion of oxygen gives rise to a mixture of the same final products as that obtained from the starting compound I (thin-layer chromatography of the acetylated reaction mixtures).

The phenylcoumarone III, which is formed in appreciable amounts, when dihydro-dehydro-diisoeugenol is treated with alkali or white liquor under pulping conditions, *viz.* without previous exclusion of air (oxygen),[8] is also obtained in high yields by the oxidation of the *o,p'*-dihydroxy-stilbene (II) with oxygen in 2 N sodium hydroxide or white liquor at 100°. Obviously, this oxidation (II→III), requiring both alkaline media and the presence of oxygen, proceeds through a radical mechanism with oxygen, hydroxy- and/or hydroperoxy radicals acting as oxidants.[9] Experimental support for this interpretation was provided by the finding that in the conversion II→III, oxygen can be replaced by potassium ferricyanide, known to be a one-electron oxidising agent.[10] The reaction may be tentatively rationalised in terms of the following steps (see Scheme 2):

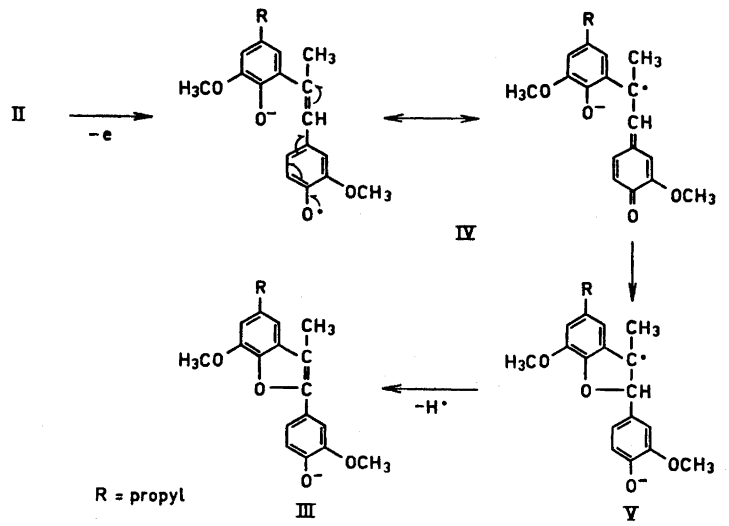
1. Formation of the mesomeric radical IV.
2. Ring closure with the formation of the phenylcoumaran-β-radical V.
3. Elimination of a hydrogen atom affording the phenylcoumarone III.

Compound III remains unaffected when treated with 2 N sodium hydroxide at 180° for 3 h.

The *o,p'*-dihydroxy-stilbene II also suffers some cleavage of the C_α-aryl, $C_{\alpha'}$-aryl, and $C_\alpha - C_{\alpha'}$-linkages giving rise to the respective degradation products (see Scheme 1): Rupture of the C_α-aryl bond results in the formation of guaiacol (VI) and α-(2-hydroxy-3-methoxy-5-propyl-phenyl)-propionaldehyde (VII) which during the working-up procedure equilibrates with its hemiacetale (VIII). To some extent these degradation products undergo condensation yielding the appropriate 1,1,2-triaryl-propane derivative (IX). Alternatively, compound IX could arise by the condensation of guaiacol with the intermediate methylene quinone formed from the *p*-hydroxy-benzyl alcohol XVI (see below) or with stilbene II. Cleavage of the $C_{\alpha'}$-aryl linkage gives 4-propylguaiacol (X) and 4-hydroxy-3-methoxy-phenylacetone (XI). Rupture of the $C_\alpha - C_{\alpha'}$ bond produces vanilline (XII) and 4-propyl-6-ethyl-guaiacol (XIII) or 4-methylguaiacol (creosol) (XIV) and 2-hydroxy-3-methoxy-5-propyl-acetophenone (XV). With the exception of the last mentioned compound all fragmentation products were separated and identified.



Scheme 1. Formation of secondary reaction products during alkaline treatment of dihydro-dehydro-diisoeugenol (I).



Scheme 2. Suggested path of formation of phenylcoumarone III from stilbene II by the action of oxygen in alkaline solution.

The formation of these cleavage products does not require the presence of oxygen and may be interpreted as to involve addition of the elements of water to the intermediate *o,p'*-dihydroxy-stilbene (II) to give compounds (XVI) and (XVII), followed by alkaline heterolysis of the carbon-carbon bonds mentioned above (reverse aldol reactions) [11,12] (see Scheme 1).

The first step received experimental support by the isolation and identification of one of the two possible addition products (XVII) (as triacetate). An intermediate, analogous to compound XVI (R = propenyl instead of propyl), in the reaction of dehydro-diisoeugenol with alkali has been postulated on the basis of NMR-data of a partially methylated derivative.[13]

Compounds II, VI, and X – XV have previously been demonstrated in the reaction mixtures obtained by the degradation of compound I with sodium hydroxide, sodium hydrogen sulphide, or sodium methyl mercaptide at a considerably higher temperature (250°) using paper chromatographic and/or gas chromatographic methods.[14,15] The formation of compounds VII, XVI, and XVII has been suggested. Alkaline cleavage of carbon-carbon bonds [11] has already been proposed to describe the degradation of compound I under these more drastic conditions.[14,15]

SUMMARY AND CONCLUSION

The results of the present work show that the *o,p'*-dihydroxy-stilbene structures, initially formed from phenolic phenylcoumaran units during alkali- and sulphate pulping may partly be converted into phenylcoumarone

structures and, to a small extent, undergo fragmentations by rupture of the C_α-aryl-, $C_{\alpha'}$-aryl-, and $C_\alpha - C_{\alpha'}$-linkages.

The formation of phenylcoumarone structures involves the loss of the phenolic hydroxyls liberated during the initial cleavage of the coumaran ring systems and, thus, counteracts the increase in alkali-solubility caused by the cleavage reaction. The blocking of these phenolic hydroxyl groups by oxidative ring closure (II→III) should also bring about a considerable stabilisation against discoloration, the potential chromophoric structures of the *o,p'*-dihydroxy-stilbene type (*e.g.* II) being converted into more stable structures of the phenylcoumarone type (*e.g.* III). On the other hand, the cleavage of $C_\alpha - C_{\alpha'}$-linkages gives rise to α-carbonyl groups, known to absorb light in near ultraviolet [16] and to induce discoloration of lignin.[17]

Although formed in small amounts only, the degradation products depicted in Scheme 1 may indicate important modes of lignin fragmentation during alkaline and sulphate pulping brought about by cleavage of carbon-carbon bonds. Recent experiments with β-aryl ether models [18] (*cf.* also Ref. 8) showed that minor fragmentation reactions of these and similar types are also given by other structures that are able to form intermediate conjugated systems.

The formation of the 1,1,2-triarylpropane (IX) illustrates reactions operating in the opposite direction, *viz.* condensations taking place between aldehydic groups, methylene quinone intermediates (*cf.* also Ref. 19) or conjugated structures [18] and reactive sites in phenolic units. A condensation reaction between formaldehyde and guaiacol, both compounds being liberated during the alkaline degradation of structural elements of the pinoresinol type, has recently [1] been reported.

EXPERIMENTAL

Melting points are corrected. Evaporations were carried out under reduced pressure.

Thin-layer (TLC)- and column chromatography. The reaction mixtures were investigated by thin-layer chromatography on silica gel HF_{254} (E. Merck AG, Darmstadt) using benzene-ethyl acetate (20:1) as solvent system (run 1 – 3 times). Iodine vapors and a 1 % solution of vanilline in conc. sulphuric acid served as developers. The preparative separations were performed by column chromatography on silicic acid (SilicAR CC-7, 100 – 200 mesh, Mallinckrodt) using the following solvent systems: chloroform, chloroform – ethyl acetate (200:1) and (25:1), diethyl ether – ligroin (3:1), and hexane – ethyl acetate in proportions between 1.5:1 and 4.5:1.

NMR-spectrometry. The NMR-spectra were run on a Perkin-Elmer R-12 spectrometer using $CDCl_3$ as solvent unless otherwise stated. The NMR-data are summarised in Table 1. Chemical shifts (δ-values) are given in ppm downfield from tetramethylsilane.

Mass-spectrometry. The mass spectra were recorded on a Perkin-Elmer 270 instrument at 20 eV using the direct inlet system or the combination with a gas chromatograph; column, silicon S-E 30 (5 %) on chromosorb W, washed with conc. hydrochloric acid and treated with dimethyldichlorosilane. The temperature of the probe heater was 150° (isotherm). Detector: 280°. The mass spectral data are given together with the other data of the compounds in the respective sections.

Model and reference compounds. The compounds used in this study were prepared as previously described (see references given below).

Cooking liquors. Aqueous solutions of sodium hydroxide (2 N), and of sodium hydroxide (3.5 g/l) and sodium sulphide ($Na_2S.9H_2O$) (3.1 g/l) ("White liquor") served as reaction media.

Treatment of dihydro-dehydro-diisoeugenol (I) with 2 N sodium hydroxide.

(a) *In nitrogen atmosphere.* Compound I, prepared from dehydro-diisoeugenol [20] by

Table 1. Proton chemical shifts (δ-values in ppm) of the products of alkaline treatment of compound I.

Compound	aromatic H	aliphatic H	methoxyl H	acetyl H	others
trans-II	6.88 (3H) (s) 6.7–6.5 (2H) (m)	6.7–6.5 ($1H_\alpha$) centred at 2.52 (2H) (tr) centred at 2.27 (3H) (d) centred at 1.65 (2H) (m) centred at 0.95 (3H) (tr)	3.87 (6H) (s)		OH 5.60 (1H) (s) OH 5.70 (1H) (s)
trans-II diacetate	7.0–6.87 (3H) (m) 6.73 (2H) (s)	6.47 ($1H_\alpha$) (b) centred at 2.59 (2H) (tr) centred at 2.19 (3H) (d) centred at 1.62 (2H) (m) centred at 0.98 (3H) (tr)	3.83 (6H) (s)	2.31 (3H) (s) 2.26 (3H) (s)	
cis-II	6.7–6.3 (5H) (m)	6.7–6.3 ($1H_\alpha$) centred at 2.46 (2H) (tr) centred at 2.14 (3H) (d) centred at 1.53 (2H) (m) centred at 0.87 (3H) (tr)	3.82 (3H) (s) 3.44 (3H) (s)		OH 5.37 (2H) (s)
cis-II diacetate	6.8–6.3 (5H) (m)	6.8–6.3 ($1H_\alpha$) centred at 2.47 (2H) (tr) centred at 2.12 (3H) (d) centred at 1.55 (2H) (m) centred at 0.87 (3H) (tr)	3.77 (3H) (s) 3.40 (3H) (s)	2.22 (3H) (s) 2.18 (3H) (s)	

Table 1. Continued.

Compound	aromatic H	aliphatic H	methoxyl H	acetyl H	others
III	7.4–6.5 (5H) (m)	centred at 2.68 (2H) (tr) 2.38 (3H) (s) 1.95–1.43 (2H) (m) 0.97 (3H) (tr)	4.00 (3H) (s) 3.95 (3H) (s)		OH 5.69 (1H) (s)
III-acetate	7.3–6.5 (5H) (m)	centred at 2.68 (2H) (tr) 2.40 (3H) (s) 1.97–1.47 (2H) (m) 0.97 (3H) (tr)	3.99 (3H) (s) 3.89 (3H) (s)	2.30 (3H) (s)	
VII	6.75–6.57 (2H) (b)	3.40–3.00 (1H) (b) centred at 2.52 (2H) (tr) centred at 1.40 (3H) (d) 1.85–1.13 (2H) (b) 0.97 (3H) (tr)	3.88 (3H) (s)		CHO 9.76 (1H) (s) OH 5.63 (1H) (s)
VII-acetate	6.8–6.5 (2H) (b)	3.70–3.30 (1H) (b) centred at 2.55 (2H) (tr) centred at 1.48 (3H) (d) 1.85–1.15 (2H) (b) centred at 0.95 (3H) (tr)	3.78 (3H) (s)	2.25 (3H) (s)	CHO 9.58 (1H) (s)
VIII-acetate	6.60 (2H) (s)	6.40 (1H) (d) 3.30 (1H) (m) 2.55 (2H) (tr) centred at 1.53 (2H) (m) centred at 1.30 (3H) (d) centred at 0.95 (3H) (tr)	3.85 (3H) (s)	2.04 (3H) (s)	

Table 1. Continued.

Compound	aromatic H	aliphatic H	methoxyl H	acetyl H	others
IX-triacetate	7.0–6.4 (8H) (m)	3.7–3.3 (2H) (b)	3.78 (3H) (s) 3.72 (3H) (s)	2.32 (3H) (s) 2.26 (3H) (s)	
		2.5–2.0 (2H) (b)	3.66 (3H) (s)	2.19 (3H) (s)	
		centred at 1.51 (2H) (b)			
		centred at 1.10 (3H) (d)			
		centred at 0.78 (3H) (tr)			
XI-acetate	7.13–6.67 (3H) (m)	3.65 (2H) (s) 2.16 (3H) (s)	3.80 (3H) (s)	2.29 (3H) (s)	
XVII-triacetate	7.00–6.20 (5H) (b)	3.25 (2H) (s)	3.78 (3H) (s)	2.33 (3H) (s)	
		centred at 2.47 (2H) (tr)	3.57 (3H) (s)	2.24 (3H) (s)	
		1.82 (3H) (s)		1.99 (3H) (s)	
		centred at 1.52 (2H) (m)			
		centred at 0.90 (3H) (tr)			

catalytic hydrogenation[21] (1.2 g) was dissolved in 2 N sodium hydroxide (45 ml) and, after replacement of the air by nitrogen, heated at 180° for 3 h (*cf.* also Ref. 5). A small sample of the resulting reaction mixture was used for direct chromatographic investigation (TLC, run twice). The rest of the solution was neutralised with carbon dioxide and extracted with chloroform.

Separation as phenols. After drying (Na_2SO_4) and evaporation the mixture of phenolic compounds was separated into 8 fractions by column chromatography (solvent system: $CHCl_3$, recovery 91 %). These fractions contained in the order of their elution (% of the total):
(1) guaiacol (VI) and the *trans*-form of compound II (3.8); (2) *trans*-form of compound II + a small amount of *cis*-form (25.7); (3) *trans*- and *cis*-forms of compound II (25.6); (4) *cis*-form of compound II(21.6); (5) compounds VII and VIII (4.0); (6–8) mixtures of several components (5.3, 5.1, and 8.7, respectively) not identified.

From fractions 2 and 4, the *trans*- and *cis*-forms of compound II, respectively, were isolated.

Separation as acetates. In another run the chloroform solution was evaporated to dryness and the residue was acetylated with acetic anhydride–pyridine (1:1) (10 ml). The mixture of acetylated phenols (1.1 g) was separated by column chromatography

(solvent system: hexane – ethyl acetate 3:1) into 13 fractions containing in the order of their elution the *acetates* of the following compounds [% weight of the total recovery (804 mg = 73 %) being given within brackets]:
(1) Compounds XIII and X (1.6); (2) Compounds X and VI (4.2); (3) Compounds X, VI, XIV, and VIII (4.1); (4) Compounds X, VI, and VII (6.8); (5) *trans-* and *cis*-forms of II (60.7); (6) *cis*-form of II (9.1); (7) *cis*-form of II and unknown compound (3.0); (8) Compound XII (3.0); (9) Compounds XII and XVII (0.6); (10) Compound XVII (4.2); (11) Compounds XVII and XI (1.0); (12) Compound XI (1.6); (13) Compound IX (4.2). Each of the fractions 1 – 4 was separated by gas chromatography and their components were identified by mass spectrometry. The acetates of compounds VII and VIII were isolated by preparative TLC from fractions 4 and 3, respectively.

1-Acetoxy-2-methoxy-benzene. MS: 166 (10), 124 (100), 109 (69), 81 (20), 53 (5).

1-Acetoxy-2-methoxy-4-methyl-benzene (acetate of XIV). MS: 180 (10), 138 (100), 123 (55), 95 (10).

1-Acetoxy-2-methoxy-4-propyl-benzene (acetate of X). MS: 208 (5), 166 (55), 138 (10), 137 (100).

1-Acetoxy-2-methoxy-4-propyl-6-ethyl-benzene (acetate of XIII). MS: 236 (10), 194 (69), 167 (15), 166 (100), 137 (5).

α-(2-Acetoxy-3-methoxy-5-propyl-phenoxy)-propionaldehyde (acetate of VII). MS: 264 (10), 222 (40), 193 (100).

2-Acetoxy-3-methyl-5-propyl-7-methoxy-coumaran (acetate of VIII). MS: 264 (10), 222 (34), 220 (68), 204 (25), 193 (100), 175 (51), 163 (20). From the fractions 5 and 6 the diacetates of the *trans-* and *cis*-forms of II, respectively, were isolated and identified by analyses, NMR, and mass spectra, as well as by m.p. (diacetate of *trans*-II).

trans-*2,4'-Diacetoxy-3,3'-dimethoxy-5-propyl-α'-methyl-stilbene.* (Diacetate of *trans*-II), m.p. 109 – 111°[5] MS: 412 (10), 370 (60), 328 (100), 299 (9), 209 (94). (Found: C 69.77; H 6.94; O 23.16. Calc. for $C_{24}H_{28}O_6$: C 69.92; H 6.79; O 23.29.)

cis-*2,4'-Diacetoxy-3,3'-dimethoxy-5-propyl-α'-methyl-stilbene.* (Diacetate of *cis*-II), oil. MS: 412 (12), 370 (52), 328 (100), 299 (6), 209 (90). (Found: C 69.72; H 6.89; 23.05. Calc. for $C_{24}H_{28}O_6$: C 69.92; H 6.79; O 23.29.)

4-Acetoxy-3-methoxy-benzaldehyde (acetate of XII) was isolated from fraction 8 and purified by sublimation under reduced pressure (1 mmHg), m.p. 77° (lit. 76°).[22]

1-(4-Acetoxy-3-methoxy-phenyl)-2-(2-acetoxy-3-methoxy-5-propyl-phenyl)-2-acetoxy-propane (Triacetate of XVII) was obtained from fraction 10 as a colorless oil. MS: 472 (2), 430 (10), 412 (12), 384 (10), 370 (95), 328 (100), 299 (5), 251 (10), 209 (40), 193 (22), 180 (20), 137 (55).

4-Acetoxy-3-methoxy-phenylacetone (Acetate of XI) was isolated from fraction 12 as yellowish crystals, m.p. 45 – 46° (lit. 45 – 47°).[23] MS: 222 (5), 180 (24), 137 (100).

1-Bis-(4-acetoxy-3-methoxy-phenyl)-2-(2-acetoxy-3-methoxy-5-propyl-phenyl)-propane (Triacetate of IX) was obtained from fraction 13 as colorless crystals: m.p. 159 – 160.5°. MS: 578 (1), 536 (3), 343 (30), 301 (66), 259 (100), 235 (25), 193 (43). (Found: C 68.43; H 6.75; O 24.75. $C_{33}H_{38}O_9$ requires: C 68.53; H 6.57; O 24.90.) MS: 578 (1), 536 (3), 343 (30), 301 (66), 259 (100), 235 (25), 193 (43).

(b) *In the presence of air (oxygen).* Compound I (1.0 g) was treated with 2 N sodium hydroxide (20 ml) as described above but without exclusion of air. Direct chromatographic investigation of the reaction mixture (TLC, run twice) showed the presence of a major component (III), of two minor components (*trans-* and *cis*-forms of II) and of small amounts of the other phenolic products, found also after alkaline treatment of I in nitrogen atmosphere (see above). After two weeks, the sodium salt of compound III (0.563 g = 53 %) was filtered off and recrystallised from chloroform, m.p. 227 – 229°. The filtrate still contained the sodium salt of compound III as the main component and smaller amounts of the other phenolic reaction products.

3-Methyl-5-propyl-7-methoxy-2-(4-hydroxy-3-methoxy-phenyl)coumarone, (III). A sample of the above sodium salt (200 mg) was dissolved in water (10 ml). The solution was neutralised with carbon dioxide and extracted with chloroform. Evaporation of the dried (Na_2SO_4) chloroform solution afforded compound III as colorless needles (153 mg = 81 %), which were recrystallised from ligroin, m.p. 86.5 – 88° (lit. 86.5 – 87.5).[20] (Found: C 73.73; H 6.88; O 19.65. Calc. for $C_{20}H_{22}O_4$: C 73.64; H 6.74; O 19.62.) MS: 326 (100), 298 (20), 297 (40), 282 (10), 175 (10), 149 (10), 137 (10), 109 (9).

Acetate: Compound III (100 mg) was acteylated with acetic anhydride (0.5 ml) in

pyridine (0.5 ml). The reaction mixture was poured into ice and the precipitate formed (98.5 mg = 87 %) was crystallised from ligroin, m.p. 122 – 124°. (Found: C 71.74; H 6.66; O 21.74. Calc. for $C_{22}H_{24}O_5$: C 71.76; H 6.52; O 21.73.) MS: 368 (19), 326 (100), 297 (26), 282 (6), 175 (4).

Compound III and its acetate did not give any depression of melting points on admixture of authentic samples prepared by dehydrogenation of compound I with sulphur [24] and acetylation of the dehydrogenation product.

In a separate experiment compound III (25 mg) was treated with 2 N sodium hydroxide (2 ml) at 180° for 3 h in the presence of air. Thin-layer chromatography of the reaction mixture showed the starting compound as the main component and only traces of unidentified reaction products.

Essentially the same reaction products were formed, when compound I was treated as described above [(a) and (b)] using white liquor instead of 2 N sodium hydroxide (TLC).

Conversion of the stilbene II into the phenylcoumarone III. (a) *With air.* The diacetate of compound II (*trans*-form) (150 mg) was dissolved in ethanol. Sodium hydroxide (2 N) (1 ml) was added and the solution was heated under reflux for 3 h. The course of the reaction was followed by TLC (run twice). The amount of compound III increased continuously at the expense of the starting material. After 3 h the reaction mixture was cooled and kept overnight. The sodium salt of compound III (95 mg, 75 %) was filtered off. A part of the sodium salt (80 mg) was acetylated (see above). The acetate (67.5 mg) was recrystallised from ligroin; m.p. 123 – 124°.

(b) *With potassium ferrieyanide.* The *trans*-form of compound II (90 mg) was dissolved in dioxan (7 ml) and 2 N sodium hydroxide (2 ml). The solution was saturated with nitrogen and a solution of potassium ferricyanide (500 mg) in 2 N potassium hydroxide (2.5 ml), also saturated with nitrogen, was added. A precipitate of the potassium salt of III was formed immediately and the total amount of stilbene II was consumed after 3 min (TLC). Compound III was purified and identified as described above.

A blank was run omitting potassium ferricyanide under otherwise identical conditions. No phenylcoumarone III was formed and the starting material was recovered.

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