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Reactions of Lignin during Sulfate Pulping. Part XIX.* Isolation and Identification of New Dimers from a Spent Sulfate Liquor

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The lipophilic portion of a neutralized spent liquor from sulfate cooking of spruce *(Picea abies)* wood meal was fractionated by conventional (CC) and improved (HPLC) liquid chromatographic techniques. In addition to previously reported degradation products (mainly monomeric compounds), a series of new dimers was isolated and identified using ^{1}H and ^{13}C NMR and mass spectroscopic methods. The formation of these dimers from prominent structures in softwood lignins is discussed in terms of degradation reactions elucidated in previous model experiments.

Most of our present knowledge about the lignin reactions taking place during sulfate pulping has been gained by studying the behaviour of appropriate model compounds under pulping conditions. By qualitative product analyses the most important mechanisms of degradation [1] and condensation [2,3] have been clarified. The mechanisms of degradation have been confirmed [4-7] by kinetic studies and the interrelationships between degradation and condensation reactions have been elucidated.[6]

It would be highly desirable to demonstrate the applicability of these results to the description of the structural changes that native lignin undergoes during sulfate pulping. This could be achieved by determining predictable structural features in the undissolved portion of the lignin ("residual" lignin) and by analyzing the resulting spent liquor for expected components of low molecular weight.

The present work is concerned with the latter approach. Pre-extracted wood meal was subjected to the conditions of sulfate pulping and the resulting spent liquor was fractionated after neutralization and freeze-drying. Sixteen lipophilic fractions were obtained and characterized using ^{1}H and ^{13}C NMR as well as GC–MS and HPLC methods. This work refers particularly to the dimeric products (*22–32*) isolated from three of these sixteen fractions by further HPLC. The remaining lipophilic and the hydrophilic fractions were not examined. With the exception of compound *22*, the dimers reported here have been isolated from a sulfate spent liquor for the first time.

RESULTS AND DISCUSSION

The monomeric and dimeric products isolated from the sulfate spent liquor are listed in Tables 1 and 2, respectively. Unless otherwise stated, the compound numbers quoted refer to the non-acetylated forms (R^1 = H in Tables 1–3).

Of the monomeric products, compounds *1–3*, *6–9*, *11–15*, *17*, *18* and *21* have been previously reported to be present in black liquors [8-10] and/or in spent liquors from sulfate cooking of milled wood lignin.[11] The formation of most of the monomeric products can be interpreted in terms of known carbon–carbon [12,13] and carbon–oxygen (alkyl aryl ether) [1] cleavage reactions. Side chains containing a carbonyl group in the α-position (in *11–13*, *17*, *18* and *21*, *cf.* also side chains in the dimeric compounds *26–30*, below) may be generated by reactions in which polysulfide ions are involved.[14,2,13]

Compounds *14–18* may originate from sulfidolytic demethylation [1] of the corresponding guaiacol derivatives, but also by aromatization of degradation products from polysaccharides. The formation of *14*, *15*, *17* and *18*, together with further phenols

* Part XVIII, see Ref. 35.

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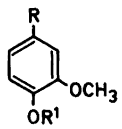
Table 1. Monomeric compounds. $R^1 = H$ or Ac.



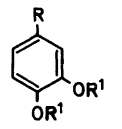
1 R = H
2 R = CH_3
3 R = C_2H_5
4 R = C_3H_7

5 R = $CH = CH_2$
6a R = $CH = CH - CH_3$ *cis*
b R = $CH = CH - CH_3$ *trans*

7 R = $CHOR^1 - CH_3$
8 R = $CH_2 - CH_2OR^1$
9 R = $CH_2 - CH_2 - CH_2OR^1$

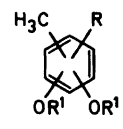
10 R = $CH = CH - CH_2OR^1$

11 R = CHO
12 R = $CO - CH_3$
13 R = $CO - CH_2 - CH_3$

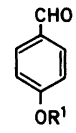


14 R = H
15 R = CH_3
16 R = C_2H_5

17 R = CHO
18 R = $CO - CH_3$



19 R = H
20 R = CH_3 (4 isomers)



21

of type *19* and *20* and enones, on treatment of D-xylose and D-glucose with 0.63 M sodium hydroxide at 96 °C has recently been demonstrated.[15]

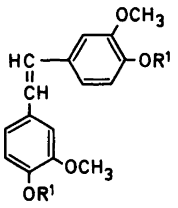
The possible contribution of catechol structures as leuco chromophores to the colour formation in sulfate pulps,[16,1] and the significance of units containing an α-carbonyl group as sensitizing group in the photo-induced yellowing of wood and pulps[17-20] have been repeatedly discussed.

Among the *dimeric compounds* hitherto identified, *trans*-4,4'-dihydroxy-3,3'-dimethoxystilbene (*22*) was present in the largest amount. It has been known for a long time that this compound is formed on alkaline treatment of lignosulfonic acids[21] and wood,[22] as well as on sulfate pulping of wood.[23] Several years ago the isolation of *22* from the spent liquor after sulfate cooking of milled wood lignin was reported.[11] The formation of *22* from 1,2-diarylpropane-1,3-diol structures has been previously[16,24,1,11] proposed. The remaining dimeric compounds have not been isolated from sulfate spent liquors before. In addition to the 4,4'-dihydroxy-3,3'-dimethoxystilbene (*22*), the 2',4-dihydroxy-3,3'-dimethoxystilbenes *23*–*27* were found. These stilbenes may be formed from phenolic arylcoumaran structures by alkali-promoted opening of the five-membered coumaran ring, followed by formaldehyde elimination from the resulting quinone methide[25] (*cf.* also Refs. 26, 16 and 1).

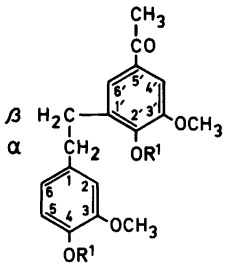
Apparently, the alkaline conversion of phenolic arylcoumaran and 1,2-diarylpropane-1,3-diol structures into the corresponding stilbenoid structures is a general reaction.[1,27] However, dissolution of the resulting stilbene into the cooking liquor presupposes the absence of any carbon–carbon bond between the position(s) *ortho* to the phenolic hydroxyl group(s) and the adjacent lignin unit, and, in the case of 2',4-dihydroxy-3,3'-dimethoxystilbenes (*23*–*27*), also the presence in the parent arylcoumaran structure of a side chain (R) which can be eliminated or degraded. Thus, stilbenoid structures should constitute important structural elements in dissolved and possibly also in residual lignins. Their roles as potential chromophores in sulfate lignins[16,1] and as intermediates in the reactions under certain pulping conditions[28,29] have previously been discussed.

An alternative route to the formation of stilbenes *22*–*27* could involve condensation of phenolic β-aryl ether structures with the appropriate phenol, followed by a 1,2-aryl migration resulting in β-aryl ether cleavage, and subsequent formaldehyde

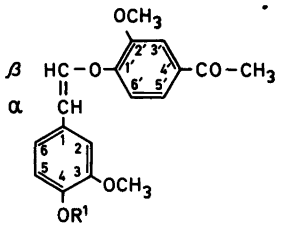
Table 2. Dimeric compounds. $R^1 = H$ or Ac.



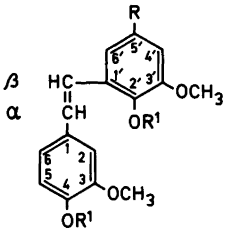
22 trans

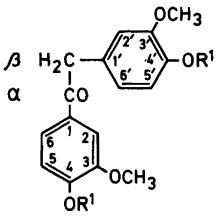


28



30 a cis
30 b trans





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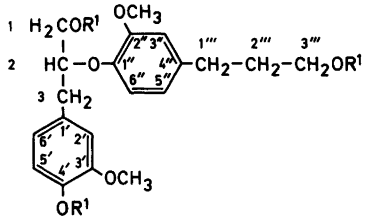
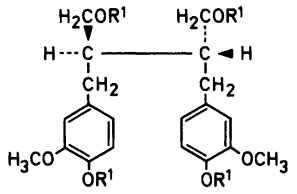


31

23 a R = H, *cis*
b R = H, *trans*
24 R = CH_3, *cis*
25 R = $CH_2-CH_2-CH_2OR^1$, *trans*
26 R = CHO
27 R = $CO-CH_3$



32

elimination.[30] The assumption that stilbenoid structures may also arise from structural elements, which *a priori* do not contain an aryl−C−C−aryl skeleton has recently[31] received experimental support. When wood meal was treated with alkali or white liquor in the presence of 2,6-xylenol, the expected stilbene, 4,4'-dihydroxy-3',5'-dimethyl-3-methoxystilbene, was formed. The relative importance of the two different ways of stilbene formation has not been determined.

The 1,2-diarylethane derivative *28* and desoxyvanilloin (*29*) have the same aryl−C−C−aryl skeleton as present in stilbenes but differ from the latter by their stages of oxidation. A possible route of formation of these compounds could therefore involve redox reactions of the corresponding stilbenes. However, attempts to support this assumption by appropriate model experiments have not been successful.

The genesis of the β-aroxy styrene *30* can be explained by alkaline conversion of the corresponding β-aryl ether structure to the quinone methide, followed by elimination of the terminal hydroxymethyl group as formaldehyde.[26,32] Under the conditions of sulfate pulping, the formation of products of the β-aroxy styrene type should be effectively suppressed by the competing sulfidolytic cleavage of the β-aryl ether linkage.[33,34] The isolation of *30* shows that this cleavage does not completely eliminate the formation of β-aroxy styrene structures (*cf.* Ref. 6). However, a considerably higher yield of β-aroxy styrenes should be expected when the alkaline treatment of wood meal is carried out in the absence of hydrosulfide, *i.e.* under the conditions of soda pulping.

In analogy to 2',4-dihydroxy stilbenes (see above), β-aroxy styrenes are, of course, only separated from lignins and lignin fragments if they are not attached

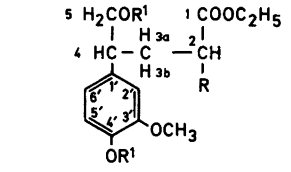
by carbon–carbon bonds from the position(s) *ortho* to the free and etherified phenolic hydroxyl group(s) to adjacent lignin units, and if the side chain of the aroxy substituent in the parent β-aryl ether structure can be eliminated or degraded. The last-mentioned structural requirement is met, *e.g.* in β-aryl ether structures in which the β-aroxy substituent is of the phenacyl-β-aryl ether type. Such substituents are in part converted into the corresponding (etherified) acetoguaiacone structures.[35]

Compound *31* should originate from phenolic β-aryl ether units lacking an α-substituent (hydroxyl, alkoxyl or aroxyl group) which can be eliminated. In such units, quinone methide formation and subsequent formaldehyde elimination or sulfidolytic cleavage of the β-aryl ether bond is precluded. Phenolic units of the β-aryl ether type containing a methylene group in the α-position could be thought to arise in a side reaction by reduction of the corresponding quinone methide intermediates. The facile reduction of benzyl aryl ether structures by sodium borohydride suggested to proceed *via* quinone methide[36] lends support to this view.[11] Moreover, compound *31* has previously been isolated from the ether soluble fraction of the reaction mixture obtained by catalytic hydrogenolysis of Ezomatsu *(Picea jezoensis)* wood meal.[37] However, phenolic products containing a methylene group in the α-position have also been found after degradation of lignins in non-reducing media[38] (*cf.* also compound *32*, below). This would indicate a second possibility of formation of compound *31*, *i.e.* from β-aryl ether structures originally containing a methylene group in the α-position.[11,39] The question whether the methylene group is originally present or formed by reduction or disproportionation remains unresolved. On further alkaline degradation involving formation of a β,γ-oxirane[26] and liberation of *9*, compound *31* would be expected to give rise to 3-(4-hydroxy-3-methoxyphenyl)-propane-1,2-diol. In fact, the latter compound has been isolated from the hydrophilic fraction obtained after alkaline treatment of milled wood lignin.[11]

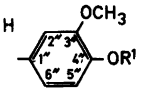
The most probable source of compound *32* are β–β linked structures, suggested to be present in small amounts in softwood lignins.[39] Comparison of the ^{1}H NMR data of compound *32* (R^1=Ac) with those of the compound obtained by catalytic hydrogenation of optically inactive pinoresinol[38] followed by acetylation showed that *32* (R^1=Ac) has the (2*R*,3*R*), (2*S*,3*S*) configuration (*cf.* Ref. 40). As in the case of compound *31*, the methylene group(s) in the α-position of *32* could be thought to arise by reduction of the corresponding quinone methide intermediate(s). Compound *32* (in optically inactive form) has also been obtained by catalytic hydrogenolysis of wood meal.[41] However, treatment of *d,l*-pinoresinol, a model for β–β linked structures in softwood lignins, with white liquor under the conditions of sulfate pulping did not yield any *32* (*cf.* also Ref. 42). Therefore, it seems more likely that *32* originates from β–β linked structures, originally containing reduced benzyl positions (*cf.* also origin of *31*, above). The isolation of 2,3-divanillyl-tetrahydrofurane, presumably a secondary product from *32*, after acidolysis,[38] supports this view.

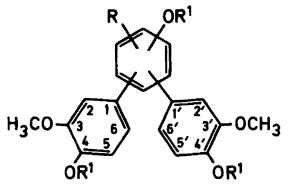
The origin of compounds *33*–*36* listed in Table 3 is obscure. The carbon skeleton in *33* and *34* and the substitution pattern of the central aromatic ring in *35* and *36* indicate that these compounds may be formed by condensation between lignin and carbohydrate degradation products. However, preliminary model experiments using appropriate condensation partners did not yield these compounds.[43] Further analytical and synthetic studies are required to elucidate the structure and formation of these products. The isolation of *33* and *34* from the lipophilic fraction of the spent liquor may be

Table 3. Further compounds. R^1=H or Ac.



33 R = H

34 R =  (2 isomers, *a* and *b*)



35 R = H

36 R = CH_3 (2 isomers, *a* and *b*)

ascribed to the fact that the parent acids (H instead of C_2H_5) are present in the form of their δ-lactones after neutralization of the original reaction mixture. Esterification of the carboxylic group should be due to reaction with the ethyl acetate (transesterification) during chromatography.

CONCLUDING REMARKS

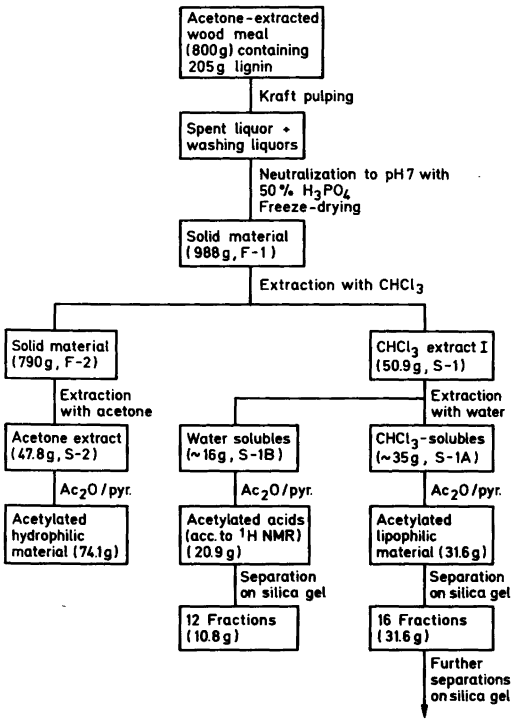
Although only a small number of fractions from a sulfate spent liquor have been examined so far, the results allow us to draw the following conclusions:

(1) Almost all monomeric and dimeric compounds isolated contain a methylene (or methyl) group, a carbonyl group, or a (ring-conjugated) double bond in the α-position. These groups render the compounds sufficiently resistent to further alkaline degradation and/or condensation. They may in part be originally present, in part be generated by alkali- and (poly)sulfide-promoted reactions during the pulping process.

(2) The formation of the majority of the identified products can be interpreted in terms of known types of reactions, given by the most prominent structures in softwood lignins and their degradation products. In particular, the formation of the dimeric products *22–32* can be explained by mechanisms previously suggested[1a] on the basis of results from model experiments. Thus, the isolation of these compounds constitutes evidence for the correctness of these mechanisms. Conversely, provided these mechanisms are accepted, the isolation of the dimeric products lends an independent support for the occurrence of β-aryl ether, arylcoumaran, 1,2-diarylpropane-1,3-diol and $\beta-\beta$ linked structures. The alkaline (and sulfidolytic) degradation of lignin, if systematically studied by extended analyses of spent liquors, could therefore represent a valuable complement to other degradation methods in the demonstration of particular structural elements in lignins.

(3) Some of the monomeric products and compounds *35* and *36* indicate that aromatization reactions take place in which carbohydrate degradation products may be involved.

(4) It seems reasonable to assume that certain structural features of the identified degradation products in the spent liquor may also be encountered from the corresponding residual lignins. The results of this work and of forthcoming analytical studies of the remaining fractions can therefore be expected to facilitate the elucidation of the structural features of residual sulfate lignins.



Scheme 1. Fractionation of the spent liquor from kraft pulping of acetone-extracted wood meal *(Picea abies)*.

EXPERIMENTAL

In this section, the compound numbers quoted refer to the acetylated forms (R^1=Ac in Tables 1–3).

The work-up and fractionation procedure described below is outlined in Scheme 1. Acetone-extracted spruce wood meal *(Picea abies)* (800 g, dry weight 746 g, containing 205 g Klason lignin) was subjected to kraft pulping conditions (wood:liquor ratio 1:10, $[HO^-]_{eff}=0.61$, $[HS^-]=0.09$). The pulp (yield 45.9 %, kappa number 20.7) was collected in a Büchner funnel and washed by slurrying in a minimal amount of 0.1 M sodium hydroxide. The spent liquor and washing liquors were combined and neutralized (pH-paper) with 50 % H_3PO_4. Hydrogen sulfide liberated during neutralization was removed from the combined

liquors using a water aspirator. Freeze-drying of the solution afforded a residue (988 g, F-1) which was extracted in portions with chloroform (total volume 8 l) at room temperature overnight with magnetic stirring. The combined chloroform extracts were evaporated under reduced pressure to give a brown-reddish oil (50.9 g, S-1). The residue from the chloroform extraction (790 g, F-2) was extracted with acetone (4 l) to yield a soluble fraction (47.8 g, S-2) and a residue (742 g). The chloroform-soluble brown reddish oil (S-1) was redissolved in chloroform and extracted with water to give a water-soluble fraction (16 g, S-1B) and a chloroform-soluble fraction (35 g, S-1A).

Fractions S-1A, S-1B and S-2 were acetylated by dissolving in a mixture of acetic anhydride and pyridine (5 ml of each per g of material) and keeping the solutions at room temperature overnight. Usual work-up of the acetylation mixture from S-1A gave acetylated S-1A (31.6 g). The other two acetylation mixtures were evaporated azeotropically with toluene yielding acetylated S-1B (20.9 g) and acetylated S-2 (74.1 g). These mixtures of acetylated compounds were characterized by ^{13}C and ^{1}H NMR spectroscopy. The decrease in weight on acetylation of S-1A, instead of the expected increase, may be due to the loss of acids in the washing step (*cf.* the isolation of *33* and *34* from the reaction mixture).

Acetylated S-1A and S-1B were chromatographed on silica gel (see below), acetylated S-1A giving 16 fractions (total weight 31.6 g) and acetylated S-1B yielding 12 fractions (total weight 10.8 g). The fractions from acetylated S-1B were characterized by ^{1}H NMR spectroscopy but were not further investigated. The fractions from acetylated S-1A were examined by ^{1}H NMR, ^{13}C NMR, GC-MS and HPLC. Further separations of fractions 2–5 afforded compounds *1*–*21*, and of fractions 6, 8 and 10 compounds *22*–*36* (*cf.* Fig. 1).

Chromatographic methods. The chromatographic methods used have been described earlier.[13] Only details specific for the present work will be given here.

Analytical HPLC. Separations were carried out on a Waters instrument using a linear gradient of 3 % to 43 % of ethyl acetate in light petroleum (60–71 °C).

Preparative LC. The first preparative separations of the components of acetylated S-1A and S-1B were performed on a Merck Lobar column size C. Acetylated S-1A was divided into 5 portions (each about 6 g) and S-1B into 3 portions (each about 7 g) and the portions were separated using a linear gradient of 10 % to 50 % ethyl acetate in light petroleum (60–71 °C) and a flow rate of 9.0 ml/min. The gradient run time was 10 h, corresponding to a

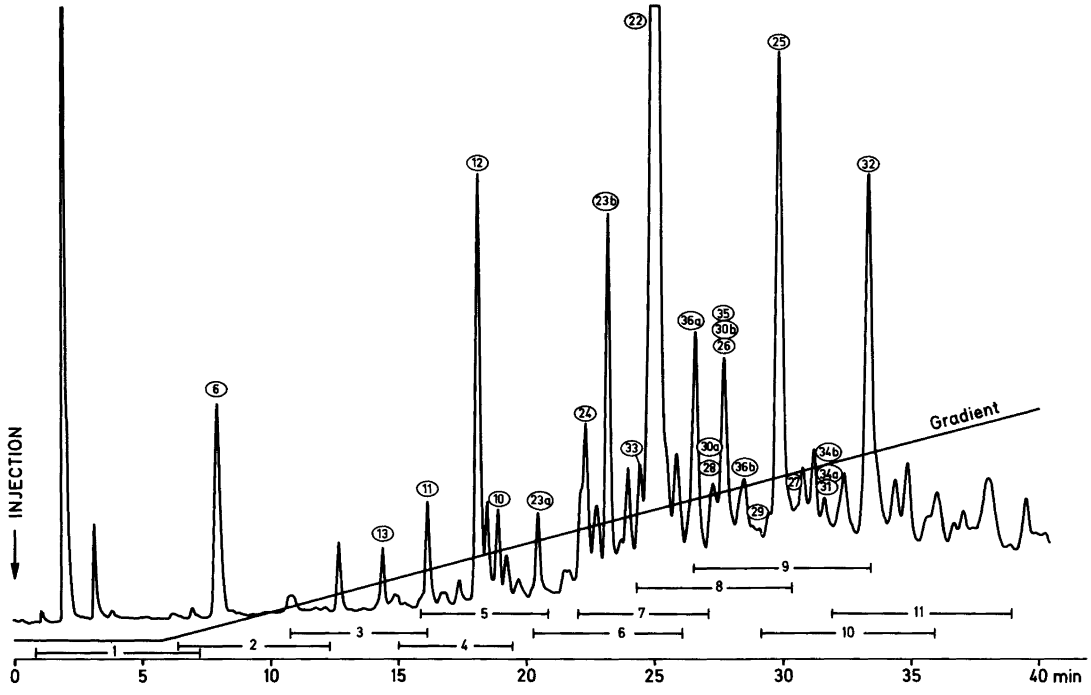


Fig. 1. HPLC chromatogram of the mixture of acetylated phenols obtained from a spent sulfate liquor

run volume of about 20 times the void volume. The fractions of 13.5 ml were collected using an LKB Ultrorac fraction collector. The separations were monitored by an LKB Uvicord II UV-detector at 280 nm. The fractions were combined according to the preparative and analytical chromatograms. The components of three of the combined fractions from the separation of S-1A (S-1A6, 1.27 g; S-1A8, 1.99 g; S-1A10, 1.30 g) were further separated on a Merck Lobar column size B with suitable linear gradients of ethyl acetate in light petroleum (60–71 °C), determined from the analytical chromatograms of the fractions. The fractions so obtained were combined according to the analytical chromatograms (detector UV 280 nm) and their components were separated by recycling on an Altex column 10 × 250 mm packed with LiChrosorb 5 μm silica gel. A Waters R 401 RI-detector was used to follow the separation. Usually 12–14 cycles corresponding to a total column length of 3–3.5 m were needed to obtain pure compounds. Separation of *34a* and *34b* required 26 cycles (6.5 m of column length).

Spectroscopy. Mass spectra were obtained on a Finnigan 3200 F instrument with data system 6000. Samples were introduced by a direct inlet system. Spectra were taken using an ion energy of 40 eV. ^{1}H and ^{13}C NMR spectra were performed using a Varian CFT-20 spectrometer. Deuteriochloroform ($CDCl_3$) was used as solvent in NMR spectroscopy unless otherwise stated. ^{1}H NMR spectra have been interpreted as first and higher order spectra.[44] When possible, *cis* and *trans* configurations have been assigned on the basis of coupling constants.

In certain cases, complete assignment of signals in the ^{13}C NMR spectra[45] was difficult due to small differences in the chemical shifts for corresponding carbons of different nuclei in dimers (*e.g.* in *25* and *34–36*). The use of shift parameters[45] was not sufficient to enable assignment. When possible, complete assignments have been made from proton noise and "off-resonance"-decoupled spectra by comparison with published[46] and unpublished[47] reference spectra. In ambiguous cases, the shifts are denoted by an asterisk (*). For the spectra not fully assigned, the number and shifts of the signals support the proposed structures.

Product identification

cis-*2',4-Diacetoxy-3,3'-dimethoxystilbene* (23a), amorphous.[27] MS *m/e* (rel. int.): 356 (M, 20), 314 (M−42, 40), 272 (M−2×42, 100), 197 (14), 169 (15), 152 (14), 151 (70), 149 (17). ^{1}H NMR.[27] δ 2.24 and 2.26 [2×s, 2×3 H, 2×φOAc], 3.50 and 3.79 [2×s, 2×3 H, 2×OCH_3], 6.43 [d, 1 H, ol, $J_{\alpha,\beta}$ 12 Hz], 6.57 [d, 1 H, ol, $J_{\alpha,\beta}$ 12 Hz], 6.60–7.10 [m, 6 H, ar]. ^{13}C NMR: δ 20.4 and 20.6 (φOCOCH_3), 55.6 and 56.0 (OCH_3), 111.2 and 113.2 (C-2 and C-4'), 121.8, 122.1 and 122.4 (C-5, C-6 and C-6'), 124.8 (C-5'), 126.2 and 131.8 (C-α and C-β), 132.3 (C-1'), 135.3 (C-1), 138.2 and 139.1 (C-4 and C-2'), 150.6 and 151.7 (C-3 and C-3'), 168.6 and 168.8 (φO*C*OCH$_3$).

trans-*2',4-Diacetoxy-3,3'-dimethoxystilbene* (23b), m.p. 138–139 °C.[27] MS *m/e* (rel. int.): 356 (M, 19), 314 (M−42, 42), 272 (M−2×42, 100), 211 (11), 197 (20), 183 (11), 169 (20), 141 (11). ^{1}H NMR, see Ref. 27. ^{13}C NMR: δ 20.5 and 20.6 (φOCOCH_3), 56.0 (OCH_3), 110.7 (C-2), 111.8 (C-4'), 118.1 (C-6'), 119.3 (C-6), 122.5 (C-5'), 123.0 (C-5), 126.4 and 130.9 (C-α and C-β), 131.2 (C-1'), 136.4 (C-1), 137.8 (C-2'), 139.7 (C-4), 151.3 (C-3), 151.6 (C-3'), 168.7 and 168.9 (φO*C*OCH$_3$).

cis-*2',4-Diacetoxy-3,3'-dimethoxy-5'-methylstilbene* (24), m.p. 116–117 °C. MS *m/e* (rel. int.): 370 (M, 9), 328 (M−42, 34), 286 (M−2×42, 100), 225 (9), 162 (11), 151 (14), 149 (9), 137 (10). ^{1}H NMR: δ 2.25 [s, 3 H, φCH_3], 2.30 [s, 6 H, 2×φOAc], 3.82 and 3.85 [2×s, 2×3 H, 2×OCH_3], 6.69 and 6.74 [2×d, 2×H, ol, $J_{\alpha,\beta}$ 8.4 Hz], 6.85–7.10 [m, 5 H, ar]. ^{13}C NMR: δ 17.8 (φCH_3), 20.7 (φOCOCH_3), 56.0 (OCH_3), 110.6 and 113.5 (C-2 and C-4'), 118.6 (C-6), 121.6 (C-6'), 122.6 (C-α or C-β, C-5 and C-1'), 127.5 (C-α or C-β), 137.1 and 137.5 (C-1 and C-5'), 138.6 and 139.3 (C-4 and C-2'), 143.0 (C-3'), 150.9 (C-3), 169.1 (φO*C*OCH$_3$).

2',4-Diacetoxy-5'-(3-acetoxypropyl)-3,3'-dimethoxystilbene (25), crude melting point 103–107 °C (lit.[25] 121.5–122 °C). MS *m/e* (rel. int.): 456 (M, 10), 414 (M−42, 26), 372 (M−2×42, 100), 364 (6), 312 (M−2×42−60, 5), 283 (5), 151 (7), 137 (12). ^{1}H NMR: δ 1.85–2.25 [m, 2 H, H-2''], 2.04 [s, 3 H, ROAc], 2.29 and 2.33 [2×s, 2×3 H, 2×φOAc], 2.70 [t, 2 H, H-1'', $J_{1'',2''}$ 7.6 Hz], 3.80 and 3.84 [2×s, 2×3 H, 2×OCH_3], 4.11 [t, 2 H, H-3'', $J_{2'',3''}$ 6.4 Hz], 6.60 and 6.76 [2×d, 2×H, H-α and H-β, $J_{\alpha,\beta}$ 10.4 Hz], 6.85–7.20 [approx. 2×s, 5 H, ar]. ^{13}C NMR: δ 20.5 and 20.6 (φOCOCH_3), 20.9 (ROCOCH_3), 30.2 (C 2''), 32.5 (C 1''), 56.0 (OCH_3), 63.9 (C-3''), 110.8 and 111.7 (C-2 and C-4'), 117.8 and 119.3 (C-6 and C-6'), 122.6* and 123.0* (C-1' and C-5'), 125.3 (C-5), 128.3 and 129.1 (C-α and C-β), 130.8* (C-1), 136.4 and 139.7 (C-4 and C-2'), 151.3 and 151.4 (C-3 and C-3'), 168.8 and 169.0 (φO*C*OCH$_3$), 171.1 (RO*C*OCH$_3$).

2',4-Diacetoxy-5'-formyl-3,3'-dimethoxystilbene (26), m.p. 156–157 °C. MS *m/e* (rel. int.): 384 (M, 20), 342 (M−42, 64), 300 (M−2×42, 100), 239 (26), 211 (13), 197 (11), 151 (21), 137 (15). ^{1}H NMR: δ 2.30 and 2.37 [2×s, 2×3 H, 2×φOAc], 3.86 and 3.88 [2×s, 2×3 H, 2×OCH_3], 6.60–7.25 [m, 5 H, ol and ar], 7.35 and 7.72 [2×d, 2×H, H-4' and H-6', $J_{4',6'}$ 1.7 Hz], 9.92 [s, H, C*H*O].

2',4-Diacetoxy-5'-acetyl-3,3'-dimethoxystilbene (27), amorphous. MS *m/e* (rel. int.): 398 (M, 5),

356 (M−42, 29), 314 (M−2×42, 100), 299 (11), 281 (16), 239 (40), 211 (23), 193 (21), 168 (24), 151 (16). ^{1}H NMR: δ 2.30 and 2.36 [2×s, 2×3 H, 2×ϕOAc], 2.62 [s, 3 H, ϕCOCH_3], 3.86 and 3.87 [2×s, 2×3 H, 2×OCH_3], 6.65−7.20 [m, 5 H, ol and ar], 7.44 and 7.79 [2×d, 2×H, H-4′ and H-6′, $J_{4',6'}$ 2.0 Hz].

1-(2-Acetoxy-5-acetyl-3-methoxyphenyl)-2-(4-acetoxy-3-methoxyphenyl) ethane (28), m.p. 133−133.5 °C. MS *m/e* (rel. int.): 400 (M, 3), 358 (M−42, 15), 316 (M−2×42, 9), 301 (1), 180 (16), 179 (18), 164 (9), 137 (100). ^{1}H NMR: δ 2.27 and 2.29 [2×s, 2×3 H, 2×ϕOAc], 2.50 [s, 3 H, ϕCOCH_3], 2.70−3.30 [m, 2×2 H, H-α and H-β], 3.76 [s, 6 H, 2×OCH_3], 6.50−6.95 [m, 4 H, ar], 7.42 [s, H, H-4′ or H-6′]. ^{13}C NMR: δ 20.6 (ϕOCOCH_3), 29.2 (ϕCOCH_3), 37.0 and 37.8 (C-α and C-β), 56.0 (OCH_3), 113.3 (C-2), 115.6 (C-4′), 120.9 (C-6), 122.4 (C-5), 125.2 (C-6′), 129.2 (C-1′), 137.2 (C-2′), 138.1 (C-4), 140.8 (C-1), 142.9 (C-5′), 150.8 (C-3), 153.4 (C-3′), 168.8 and 169.1 (ϕOCOCH$_3$), 198.7 (ϕCOCH$_3$).

Desoxyvanilloin diacetate (29), amorphous. MS *m/e* (rel. int.): 372 (M, 0.4), 330 (M−42, 4), 288 (M−2×42, 1) 193 (15), 151 (100), 137 (22), 123 (10). ^{1}H NMR: δ 2.27 and 2.30 [2×s, 2×3 H, 2×ϕOAc], 3.78 and 3.84 [2×s, 2×3 H, 2×OCH_3], 4.20 [s, 2 H, H-β], 6.67−6.97 [m, 3 H, ar], 7.08 [d, H, H-5, $J_{5,6}$ 8.6 Hz], 7.57 [dd, H, H-6, $J_{2,6}$ 1.9 Hz, $J_{5,6}$ 8.6 Hz], 7.57 [d, H, H-2, $J_{2,6}$ 1.9 Hz]. ^{13}C NMR: δ 20.5 (ϕOCOCH_3), 45.2 (C-β), 56.1 (OCH_3), 112.4 (C-2), 113.7 (C-2′), 121.8 (C-6′), 122.0 (C-6), 123.0 (C-5 and C-5′), 133.3 (C-1′), 135.5 (C-1), 139.2 (C-4′), 144.3 (C-4), 151.4 (C-3′), 151.7 (C-3), 168.3 and 168.8 (ϕOCOCH$_3$), 196.1 (C-α).

cis-*β-(4-Acetyl-2-methoxyphenoxy)-4-acetoxy-3-methoxystyrene (30a)*, amorphous. MS *m/e* (rel. int.): 356 (M, 24), 314 (M−42, 100), 243 (13), 228 (12), 211 (27), 165 (48), 151 (18), 149 (22). ^{1}H NMR: δ 2.28 [s, 3 H, ϕOAc], 2.57 [s, 3 H, ϕCOCH$_3$], 3.83 and 3.91 [2×s, 2×3 H, 2×OCH_3], 5.67 [d, H, H-α, $J_{\alpha,\beta}$ 7 Hz], 6.63 [d, H, H-β, $J_{\alpha,\beta}$ 7 Hz], 6.80−7.20 [m, 4 H, ar], ~7.51 [dd, H, H-5′, $J_{3',5'}$ 2 Hz, $J_{5',6'}$ 7 Hz], 7.57 [d, H, H-3′, $J_{3',5'}$ 2 Hz].

trans-*β-(4-Acetyl-2-methoxyphenoxy)-4-acetoxy-3-methoxystyrene (30b)*, amorphous. MS *m/e* (rel. int.): 356 (M, 25), 314 (M−42, 100), 243 (12), 228 (12), 211 (26), 151 (19), 149 (21), 133 (15). ^{1}H NMR: δ 2.29 [s, 3 H, ϕOAc], 2.57 [s, 3 H, ϕCOCH_3], 3.81 and 3.93 [2×s, 2×3H, 2×OCH_3], ~6.38 [d, H, H-α, $J_{\alpha,\beta}$ 12 Hz], 6.65−7.15 [m, 4 H, H-β and ar], ~7.07 [d, H, H-5′, $J_{5',6'}$ ~8 Hz], ~7.54 [dd, H, H-5′, $J_{3',5'}$ ~2 Hz, $J_{5',6'}$ ~8 Hz], 7.57 [d, H, H-3′, $J_{3',5'}$ ~2 Hz].

3-(4-Acetoxy-3-methoxyphenyl)-2-[4-(3-acetoxypropyl)-2-methoxyphenoxy]propyl acetate (31), amorphous. MS *m/e* (rel. int.): 488 (M, 1.1), 265 (32), 223 (5), 205 (10), 189 (3), 163 (100), 151 (4), 131 (48). ^{1}H NMR, see Ref. 37. ^{13}C NMR: δ 20.6 (ϕOCOCH_3), 20.9 (ROCOCH_3), 30.3 (C-2‴), 31.9 (C-1‴), 38.1 (C-3), 56.0 (OCH_3), 63.8 (C-3‴), 65.1 (C-1), 79.2 (C-2), 113.0 and 114.1 (C-2′ and C-3″), 118.6 and 120.7 (C-6′ and C-5″), 121.7 and 122.6 (C-5′ and C-6″), 136.2 and 136.5 (C-1′ and C-4″), 138.7 (C-4′), 145.7 (C-1″), 151.0 (C-3′ and C-2″), 169.0 (ϕOCOCH$_3$), 170.8 (ROCOCH$_3$).

(2R,3R),(2S,3S)-2,3-Divanillyl-1,4-butandiol tetraacetate (32), amorphous.[48] MS *m/e* (rel. int.): 530 (M, 0.3), 488 (M−42, 6), 446 (M−2×42, 8) 428 (M−42−60, 2), 386 (M−2×42−60, 7), 326 (M−2×42−2×60, 4), 189 (28), 176 (15), 163 (7), 151 (9), 137 (100), 131 (8). ^{1}H NMR, see Ref. 40. ^{13}C NMR, see Ref. 49.

Ethyl 5-acetoxy-4-(4-acetoxy-3-methoxyphenyl)-pentanoate (33), amorphous. MS *m/e* (rel. int.): 352 (M, 0.7), 307 (M−45, 3), 292 (M−60, 7), 250 (M−60−42, 100), 177 (49), 163 (22), 150 (19), 145 (75), 131 (30). ^{1}H NMR: δ 1.21 [t, 3 H, −OCH$_2$CH_3, J 7.2 Hz], 2.00 [s, 3 H, ROAc], 2.00−2.35 [m, 2×2 H, H-2 and H-3], 2.28 [s, 3 H, ϕOAc], 2.70−3.10 [m, H, H-4, $J_{4,5}$ 6.9 Hz], 3.79 [s, 3 H, OCH_3], 4.07 [q, 2 H, −OCH_2CH$_3$, J 7.2 Hz], 4.17 [d, 2 H, H-5, $J_{4,5}$ 6.9 Hz], 6.69 [dd, H, H-6′, $J_{2',6'}$ 2 Hz, $J_{5',6'}$ 9 Hz], 6.74 [d, H, H-2′, $J_{2',6'}$ 2 Hz], 6.93 [d, H, H-5′, $J_{5',6'}$ 9 Hz]. ^{13}C NMR: δ 14.2 (−OCH$_2$CH$_3$), 20.6 (ϕOCOCH_3), 20.9 (ROCOCH_3), 27.7 (C-3), 32.0 (C-2), 44.3 (C-4), 56.0 (OCH_3), 60.4 (−OCH$_2$CH$_3$), 68.0 (C-5), 112.1 (C-2′), 120.0 (C-6′), 122.9 (C-5′), 138.9 (C-4′), 139.6 (C-1′), 151.2 (C-3′), 168.9 (ϕOCOCH$_3$), 170.9 (ROCOCH$_3$), 173.2 (C-1).

Ethyl 5-acetoxy-2,4-bis(4-acetoxy-3-methoxyphenyl)-pentanoate (34a), amorphous. MS *m/e* (rel. int.): 516 (M, 1), 474 (M−42, 9), 414 (M−42−60, 11), 372 (M−2×42−60, 45), 326 (11), 299 (58), 248 (32), 209 (72), 175 (55), 150 (100), 137 (95). ^{1}H NMR: δ 1.14 [t, 3 H, −OCH$_2$CH_3, J 7.1 Hz], 1.97 [s, 3 H, ROAc], 2.10−2.40 [m, 2 H, H-3], 2.28 [s, 6 H, 2×ϕOAc], 2.40−2.85 [m, H, H-4, $J_{4,5}$ 5.9 Hz], 3.36 [t, H, H-2, $J_{2,3}$ 7.7 Hz], 3.76 [s, 6 H, 2×OCH_3], 4.00 [q, 2 H, −OCH_2CH$_3$, J 7.1 Hz], 4.11 [d, 2 H, H-5, $J_{4,5}$ 5.9 Hz], 6.55−7.05 [m, 6 H, ar]. ^{13}C NMR: δ 14.0 (−OCH$_3$CH$_3$), 20.7 (ϕOCOCH_3), 20.8 (ROCOCH_3), 35.4 (C-3), 42.5 (C-4), 48.9 (C-2), 56.0 (OCH_3), 61.0 (−OCH_2CH$_3$), 68.2 (C-5), 112.6 (C-2′ and C-2″), 120.2 and 120.5 (C-6′ and C-6″), 122.9 (C-5′ and C-5″), 136.9* (C-4′ and C-4″), 139.0* and 139.2* (C-1′ and C-1″), 151.3 (C-3′ and C-3″), 168.9 (ϕOCOCH$_3$), 170.7 (ROCOCH$_3$), 173.5 (C-1).

*Ethyl 5-*acetoxy-*2,4-bis(4-acetoxy-3-methoxyphenyl)-pentanoate (34b)*, amorphous. MS *m/e* (rel. int.): 516 (M, 1), 474 (M−42, 11), 414 (M−42−60, 8), 372 (M−2×42−60, 33), 326 (11), 299 (56), 250 (50), 248 (32), 209 (76), 175 (59), 150 (100), 137 (86). ^{1}H NMR: δ 1.20 [approx. t, 3 H, −OCH$_2$CH_3], 2.01 [s, 3 H, ROAc], 2.05−2.40 [m, 2 H, H-3, $J_{2,3a}$ 4.9 Hz, $J_{2,3b}$ 10.2 Hz], 2.27 and 2.29 [2×s, 2×3 H, 2×ϕOAc], 2.40−3.00 [m, H, H-4], 3.39 [dd, H, H-2, $J_{2,3a}$ 4.9 Hz, $J_{2,3b}$ 10.2 Hz], 3.76 and 3.78

[2 × s, 2 × 3 H, 2 × OCH_3], 3.80–4.30 [m, 2 × 2-H, $-OCH_2CH_3$ and H-5], 6.55–7.10 [m, 6 H, ar]. ^{13}C NMR: δ 14.2 ($-OCH_2CH_3$), 20.6 ($\phi OCOCH_3$), 20.9 ($ROCOCH_3$), 36.7 (C-3), 43.2 (C-4), 49.0 (C-2), 56.0 (OCH_3), 61.0 ($-OCH_2CH_3$), 68.0 (C-5), 112.2 and 112.3 (C-2′ and C-2″), 120.0 (C-6′ and C-6″), 122.9 (C-5′ and C-5″), 138.0* (C-4′ and C-4″), 139.1* and 139.8* (C-1′ and C-1″), 151.3 and 152.0 (C-3′ and C-3″), 168.9 ($\phi OCOCH_3$), 169.8 ($ROCOCH_3$), 173.2 (C-1).

Bis(4-acetoxy-3-methoxyphenyl)-acetoxybenzene (35), amorphous. MS *m/e* (rel. int.): 464 (M, 4), 422 (M–42, 22), 380 (M–2 × 42, 48), 338 (M–3 × 42, 100), 323 (4), 305 (9), 295 (4). ^1H NMR [$(CD_3)_2CO$]: δ 2.11 [s, 3 H, ϕOAc], 2.25 [s, 6 H, 2 × ϕOAc], 3.85 and 3.89 [2 × s, 2 × 3 H, 2 × OCH_3], 7.00–7.50 [m, 7 H, ar], ~7.64 [dd, H, ar, J_{meta} 2.4 Hz, J_{ortho} 10.3 Hz], 7.71 [d, H, ar, J_{meta} 2.4 Hz]. ^{13}C NMR: δ 20.6 and 20.8 ($\phi OCOCH_3$), 56.0 (OCH_3), 111.7 and 113.5 (C-2 and C-2′), 119.6 and 121.4 (C-6 and C-6′), 122.7 and 123.2 (C-5 and C-5′), 123.3, 127.4 and 129.8 (*C*H in benzene ring), 134.7 (*C*-ϕ in benzene ring), 136.3* (C-1), 139.2*, 139.4* and 139.6* (C-1, C-4, C-4′ and *C*-ϕ in benzene ring), 147.4 (*C*-OAc in benzene ring), 151.0 and 151.4 (C-3 and C-3′), 169.0 and 169.4 ($\phi OCOCH_3$).

Bis(4-acetoxy-3-methoxyphenyl)-acetoxytoluene (36a), amorphous. MS *m/e* (rel. int.): 478 (M, 5), 436 (M–42, 30), 394 (M–2 × 42, 39), 352 (M–3 × 42, 100), 319 (19), 309 (7), 291 (6), 151 (9). ^1H NMR: δ 2.10 [s, 3 H, ϕOAc], 2.27 [s, 3 H, ϕCH_3], 2.32 [s, 6 H, 2 × ϕOAc], 3.82 and 3.87 [2 × s, 2 × 3 H, 2 × OCH_3], ~6.99 [approx. s, 3 H, ar], ~7.08 [approx. s, 3 H, ar], 7.36 [s, 2 H, ar]. ^{13}C NMR: δ 16.7 (ϕCH_3), 20.6 ($\phi OCOCH_3$), 56.0 (OCH_3), 111.7 and 113.5 (C-2′ and C-2″), 119.6 and 121.4 (C-6′ and C-6″), 122.6 and 123.1 (C-5′ and C-5″), 127.4 and 129.2 (*C*H in toluene moiety), 131.5[a] (*C*-ϕ in toluene moiety), 135.1[a] (*C*-CH_3 in toluene moiety), 136.8* (C-1), 138.9* and 139.4* (C-1′, C-4, C-4′ and *C*-ϕ in toluene moiety), 146.3 (*C*-OAc in toluene moiety), 150.9 and 151.4 (C-3 and C-3′), 168.9 ($\phi OCOCH_3$).

Bis(4-acetoxy-3-methoxyphenyl)-acetoxytoluene (36b), amorphous. MS *m/e* (rel. int.): 478 (M, 6), 436 (M–42, 21), 394 (M–2 × 42, 100) 352 (M–3 × 42, 20), 305 (5), 291 (12), 228 (17), 197 (11). ^1H NMR: δ 2.12 [s, 3 H, ϕOAc], 2.30 [s, 3 H, ϕCH_3], 2.32 [s, 6 H, 2 × ϕOAc], 3.88 [s, 6 H, 2 × OCH_3], 6.70–7.20 [m, 6 H, ar], 7.25–7.75 [m, 2 H, ar].

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[a] Denote that assignments may be reversed.

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