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Acid Reactions of the Lignin Model 1,2-Bis(3,4-dimethoxyphenyl)-1,3-propanediol

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1,2-Bis(3,4-dimethoxyphenyl)-1,3-propanediol on acid treatment [refluxing with 0.1 M (or 0.2 M) acid in dioxane–water (9:1)] undergoes two competing reactions: a reverse Prins reaction leading to (*E*)-3,3′,4,4′-tetramethoxystilbene (and formaldehyde) and a dehydration with formation of aryl-substituted allyl alcohols [the *E* and *Z* forms of 2,3-bis(3,4-dimethoxyphenyl)-2-propen-1-ol, 1,2-bis(3,4-dimethoxyphenyl)-2-propen-1-ol] that are comparatively slowly converted into a series of carbonyl compounds [1,2-bis(3,4-dimethoxyphenyl)-1-propanone, 2,2-bis(3,4-dimethoxyphenyl)propanal, 1,1-bis(3,4-dimethoxyphenyl)-2-propanone, 2,3-bis(3,4-dimethoxyphenyl)propanal] and 2-(3,4-dimethoxyphenyl)-5,6-dimethoxy-1*H*-indene. HBr (and to a lesser extent HCl) catalyses the formation of allyl alcohols while only traces of these compounds are formed when CH_3SO_3H is used as the catalyst [(*E*)-3,3′,4,4′-tetramethoxystilbene is the predominant reaction product]. HBr promotes the formation of 1,2-bis(3,4-dimethoxyphenyl)-1-propanone from the intermediate (*E*)-2,3-bis(3,4-dimethoxyphenyl)-2-propen-1-ol. α-Chloromethyl-3,3′,4,4′-tetramethoxystilbene and α-bromomethyl-3,3′,4,4′-tetramethoxystilbene are formed in the reactions catalysed by HCl and HBr, respectively. The preparation and/or isolation of most of the detected acidolysis products is described and their stereochemistry is elucidated. A stereoselective synthesis of *threo*-1,2-bis(3,4-dimethoxyphenyl)-1,3-propanediol involving hydroboration–oxidation of (*E*)-2,3-bis(3,4-dimethoxyphenyl)propenoic acid is reported.

From experiments with lignins and model compounds it can be concluded that 1,2-diaryl-1,3-propanediol structures (β-1 structures) in lignins (**1**) on acid treatment give rise to stilbenes of type **2** and a series of carbonyl compounds (e.g. **4**)[1–7] (Fig. 1). Analysis of lignin acidolysis products originating from such structures is of interest in connection with the characterization and structural elucidation of lignins.[2,7] Much attention has been paid to the formation of stilbenes of type **2** from lignin structures of the β-1 type during pulping processes, since such stilbenes constitute an important class of leucochromophoric groups (see e.g. Ref. 8). From the results presented in this paper it can be concluded that the formation of carbonyl compounds (e.g. **4**) (but not stilbenes of type **2**) proceeds via aryl-substituted allyl alcohols of type **3** (Fig. 1). It is noteworthy in this context that structural elements of type **3** have been suggested to be present in native lignin[9] and that model compounds representing such structural elements have been studied in connection with work dealing with the bleaching of pulp.[10,11] Syntheses reported in this paper provide a basis for the steric assignments of lignin models representative of lignin structures of type **3**.

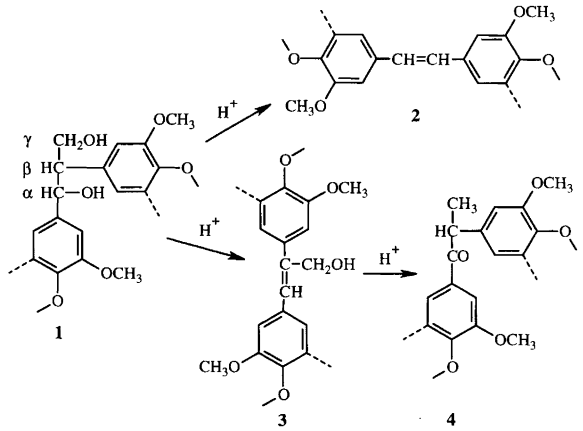
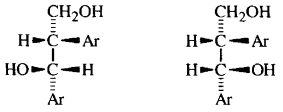


Fig. 1. Acid degradation of structural elements in lignin of β-1 type (**1**) leads to the formation of stilbenes of type **2** and carbonyl compounds (e.g. **4**).

Studies on the acid degradation of β-1 compounds

have shown that the product pattern is strongly dependent on the reaction conditions (e.g. the nature of the catalyst).[1–7] To obtain further information about the acid-catalysed reactions of structural elements in lignins of the β-1 type, we have undertaken a series of experiments with the model compound 1,2-bis(3,4-dimethoxyphenyl)-1,3-propanediol (**5**). Compound **5** was refluxed with dioxane–water (9:1) in the presence of different acid catalysts and the compositions of the reaction mixtures were analysed. The inter-relationships of the products formed were studied in separate experiments.



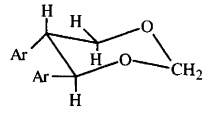
5a **5b**

Ar = 3,4-dimethoxyphenyl

In a recent investigation of acid reactions of hydrobenzoins[12] it was shown that substantial amounts of the corresponding deoxybenzoins are obtained in the presence of certain catalysts (HCl, HBr) while only traces of such compounds are formed when other acids are used as catalysts (diarylacetaldehydes are the predominant products). The catalysts used in the present study were selected on the basis of the results from the acidolysis experiments with hydrobenzoins. Acid reactions of a series of lignin structures (β-1, β-5, β-O-4) are strongly influenced by the nature of the catalyst (this is briefly discussed in the introductory section of Ref. 12). Therefore the experiments with **5** described in this work not only provide information about the acid reactions of β-1 structures but also contribute to a better understanding of the analogous reactions of other types of structural element in lignins (β-5, β-O-4).

Results and discussion

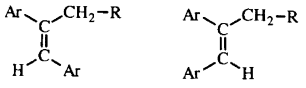
Acid reactions of 1,2-bis(3,4-dimethoxyphenyl)-1,3-propanediol. 1,2-Bis(3,4-dimethoxyphenyl)-1,3-propanediol (**5**) was refluxed with dioxane–water (9:1) for different periods of time in the presence of various acid catalysts. The obtained acidolysis products were analysed by ^{1}H NMR spectroscopy. The results are summarized in Table 1. Experiments were performed with both the *erythro-* (**5a**) and *threo-* (**5b**) forms of **5**. No differences in the reaction patterns were observed. Acidolysis of **5** for 0.5–1 h with CH_3SO_3H as the catalyst gave (*E*)-3,3′,4,4′-tetramethoxystilbene (**7**) in high yield (ca. 70%); the *Z*-form of the stilbene was not formed (^{1}H NMR). The formation of stilbene **7** in connection with the liberation of formaldehyde can be understood as a reverse-Prins reaction (Fig. 2). The acetal **16** (formed from **5** and liberated formaldehyde) and small amounts of **8**–**12** were detected in the reaction mixtures (Table 1).



16

Ar = 3,4-dimethoxyphenyl

When HBr was used as the catalyst in acidolysis experiments with **5** the yield of stilbene **7** was rather low (≈20%) (Table 1). Carbonyl compounds **11**–**14** together with the indene derivative **15** constitute the major part of the reaction products obtained on prolonged treatment (4 h); ketone **11** is the most prominent constituent (yield, ca. 28%). Rather large amounts of allyl alcohols **8**–**10**, as well as the bromides **17a** and **17b**, are present in reaction mixtures obtained when **5** is acidolysed with HBr for a short period of time (e.g. 10 min, Table 1).



17a R = Br **17b** R = Br

18a R = Cl **18b** R = Cl

Ar = 3,4-dimethoxyphenyl

The compositions of the reaction products obtained from the HBr and the CH_3SO_3H experiments differ dramatically. This might be explained by a catalytic

Table 1. Yields (determined by ^{1}H NMR spectroscopy) of products obtained on refluxing of 1,2-bis(3,4-dimethoxyphenyl)-1,3-propanediol (**5**) with dioxane–H_2O (9:1) containing acid catalysts.

Starting material	Catalyst	Reaction time	Yields (%) of identified products									
			7	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
5a	HBr (0.1 M)	4 h	18	—	—	—	28	14	4	3	11	—
5a[a]	HBr (0.1 M)	10 min	19	7	4	1	12	8	2	Trace	4	6
5a	CH_3SO_3H (0.1 M)	1 h	68	3	1	1	1	1	—	—	—	7
5b	CH_3SO_3H (0.1 M)	1 h	67	3	1	1	1	1	—	—	—	7
5a	HBr (0.2 M)	4 h	19	—	—	—	27	11	4	2	11	—
5a[b]	HCl (0.2 M)	4 h	29	1	1	Trace	12	14	4	1	8	1

[a] ^{1}H NMR spectra of the acidolysis product showed the presence of the bromides **17a** (yield, 13%) and **17b** (yield, 6%). [b] ^{1}H NMR spectra of the acidolysis product showed the presence of the chlorides **18a** (yield, 4%) and **18b** (yield, 2%).

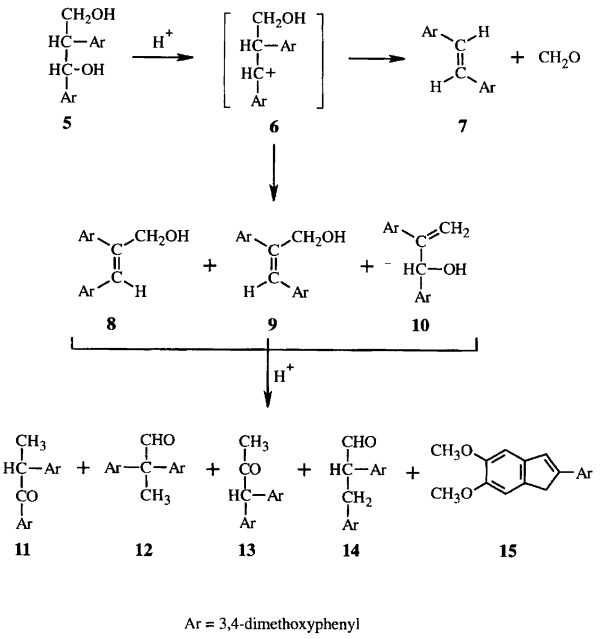


Fig. 2. Acid reactions of 1,2-bis(3,4-dimethoxyphenyl)-1,3-propanediol (**5**).

effect of the bromide ion promoting the dehydration of **5**, with formation of allyl alcohols **8–10**, and subsequent conversion of the initially formed allyl alcohols into compounds **11–15** in acid-catalysed reactions (Fig. 2). The bromides **17a** and **17b**, present at an early stage of the experiments with HBr as the catalyst, are thought to form an equilibrium mixture with the allyl alcohols. This is supported by the fact that substantial amounts of the bromides are present in the reaction mixture obtained on acidolysis (HBr) of the intermediate allyl alcohol **8** for a short period of time (10 min).

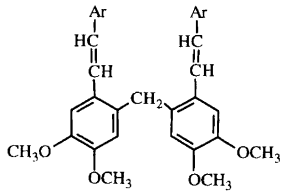
An experiment with HCl as the catalyst suggests that the chloride ion catalyses the dehydration of **5** in the same manner as the bromide ion but the catalytic effect is less pronounced (Table 1). Dehydration with formation of allyl alcohols occurs only to a very small extent in the CH_3SO_3H experiments (Table 1). To summarize, HBr catalyses the formation of allyl alcohols more efficiently than does HCl and the catalytic effect of CH_3SO_3H in this reaction is almost negligible. Interestingly, the acids used in this study exhibited the same order of efficiency as catalysts for the dehydration of hydrobenzoins leading to deoxybenzoins (HBr > HCl > CH_3SO_3H).[12] Acidolysis of hydrobenzoins involves competition between a rearrangement (a diarylacetaldehyde is formed) and a dehydration reaction leading to deoxybenzoins [ArCH(OH)CH(OH)Ar → $(Ar)_2CHCHO + ArCOCH_2Ar$] while a reverse-Prins reaction competes with dehydration resulting in the formation of allyl alcohols **8–10** in the acidolysis of **5** (rearrangements involving the initially formed carbocation **6** were not observed) (Fig. 2).

To obtain evidence for the reaction routes proposed in Fig. 2 acidolysis experiments were performed with the proposed intermediate **8**. Results from analysis (^1H NMR) of the reaction mixtures are given in Table 2. Both HBr and CH_3SO_3H catalyse the isomerization of the allyl alcohols **8–10** (Fig. 3). Neither HBr nor CH_3SO_3H converts **8** into stilbene **7**; this is in accordance with the reaction route for the formation of stilbene **7** from **5** suggested in Fig. 2. Both HBr and CH_3SO_3H catalyse the conversion of the allyl alcohols into compounds **11–15** (Table 2, Fig. 3). However, the yields of these products are strongly dependent on the nature of the catalyst (Table 2). HBr favours the formation of ketone **11**. This could be explained by a catalytic effect of the bromide ion promoting the formation of ketone **11** from the intermediate carbocation **19** (Fig. 3). An alternative explanation for the high yield of **11** would be an acid-catalysed isomerization of aldehyde **12** (Fig. 3). To examine this possibility an acidolysis experiment (catalyst, HBr) was performed with **12**. Isomerization of **12** with formation of ketone **11** actually occurred but the the yield was low (Table 2). Accordingly, isomerization of aldehyde **12** is not the primary reason for the comparatively high yield of ketone **11** in the HBr catalysed reaction of **8** (or **5**).

Some of the compounds formed on acidolysis of **5** are described in the literature (**7**,[5] **8**,[13,14] **15**[15] and **16**[3,16]). The synthesis of acidolysis products **9**, **11**, **14**, **17a**, **17b**, **18a** and **18b** is described in this paper. Proof of the structure of the acidolysis products **12**, **13** and **10** (acetate derivative) was achieved by examination of samples of the compounds isolated from reaction mixtures obtained on acidolysis of **5** on a preparative scale. In addition to the acidolysis products discussed above small amounts of **20** were isolated from an acidolysis mixture of **5**. Compound **20** is assumed to be a condensation product of **7** and formaldehyde.

Table 2. Yields (determined by ^1H NMR spectroscopy) of products obtained on refluxing of (*E*)-2,3-bis(3,4-dimethoxyphenyl)-2-propen-1-ol (**8**) and 2,2-bis(3,4-dimethoxyphenyl)propanal (**12**) with dioxane–H_2O (9:1) containing acid catalysts.

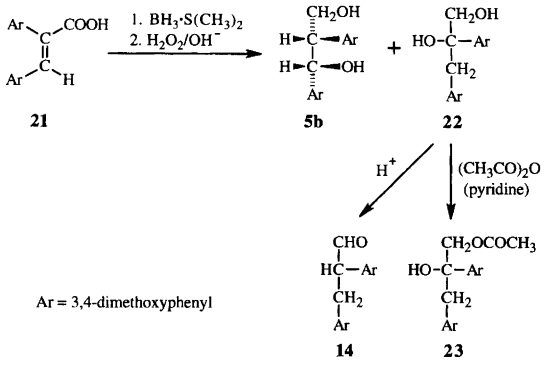
Starting material	Catalyst	Reaction time	Yields (%) of identified products								
			7	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
8	HBr (0.1 M)	4 h	—	—	—	—	35	19	5	4	16
8	CH_3SO_3H (0.1 M)	4 h	—	7	7	2	2	19	5	Trace	30
8	CH_3SO_3H (0.2 M)	30 min	—	26	15	6	Trace	9	3	Trace	22
12	HBr (0.1 M)	4 h	—	—	—	—	8	83	1	—	—



20

Ar = 3,4-dimethoxyphenyl

Synthesis of the diastereomeric forms of 1,2-bis(3,4-dimethoxyphenyl)-1,3-propanediol. The *erythro* form of the 1,2-diaryl-1,3-propanediol model examined (**5a**) was prepared according to the method described in Ref. 17. Other methods for the synthesis of **5** and related compounds[1,16,18–21] gave mixtures of the diastereomeric forms. In connection with this work a stereoselective synthesis of the *threo* form (**5b**) was developed. Hydroboration–oxidation of (*E*)-2,3-bis(3,4-dimethoxyphenyl)propenoic acid (**21**) provided sterically pure **5b** (Scheme 1). 2,3-Bis(3,4-dimethoxyphenyl)-1,2-propanediol (**22**) was obtained as a by-product. Acidolysis of **5** gave rise to small amounts of aldehyde **14** (Table 1); this acidolysis product was synthesized by acid treatment of **22**. Acetylation (acetic anhydride–pyridine) of **22** gave the monoacetate **23** (Scheme 1).



Ar = 3,4-dimethoxyphenyl

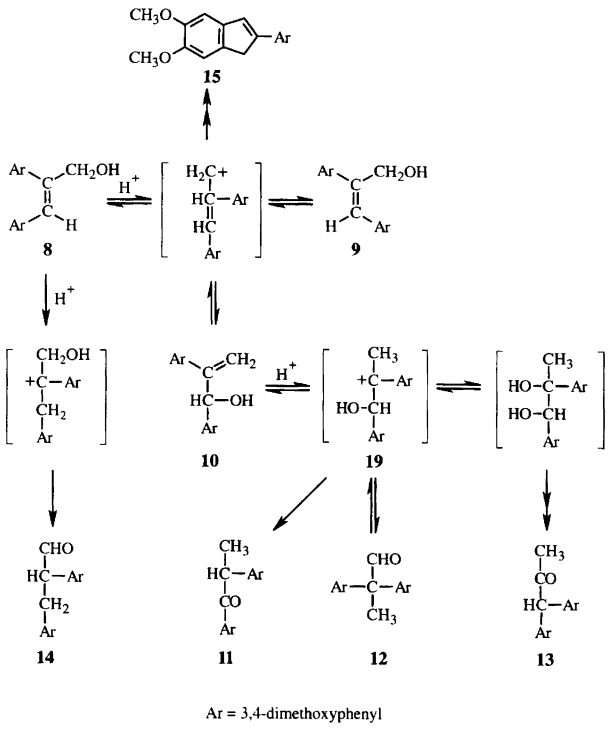
Scheme 1.

Experimental

Merck Kieselgel 60 (230–400 mesh) was used for flash chromatography. Reagent grade dioxane was distilled over Na.

^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 100.6 MHz with a Varian XL-400 (VXR-5000) instrument (temperature, ca. 20 °C). Deuteriochloroform was used as the solvent unless otherwise specified [internal reference, $(CH_3)_4Si$].

Thin layer chromatography (TLC) was carried out on silica gel plates (Merck, Kieselgel 60 F_{254}) with toluene–dioxane–acetic acid (90:25:4) (R_f values: **5b**, 0.12; **5a**, 0.13; **22**, 0.14; **8**, 0.31; **9**, 0.31; **14**, 0.44) and dichloromethane–ethyl acetate (10:1) [R_f values: **9**, 0.12; **8**, 0.14; **10**, 0.16; **16**, 0.35; **13**, 0.37; **11**, 0.47; **12**, 0.50; (*Z*)-3,3′,4,4′-



Ar = 3,4-dimethoxyphenyl

Fig. 3. Compounds detected in acidolysis mixtures of (*E*)-2,3-bis(3,4-dimethoxyphenyl)-2-propen-1-ol (**8**) and proposed reaction routes for their formation. [The formation of **14** might alternatively proceed via a protonation of (*Z*)-2,3-bis(3,4-dimethoxyphenyl)-2-propen-1-ol (**9**). Formation of **14** proceeding via carbocation **6** (but not via **8** or **9**) is also conceivable but the yields of **14** obtained (Tables 1 and 2) do not support this reaction route.]

tetramethoxystilbene, 0.54; **15**, 0.55; **7**, 0.59] as eluents. Spots were made visible with UV light and by spraying with formalin–H_2SO_4 (1:9) and subsequent heating.

(E)-2,3-Bis(3,4-dimethoxyphenyl)propenoic acid (**21**) was prepared according to Walker.[22] Its structure has been confirmed by a crystal structure determination.[23] ^{1}H NMR (DMSO-d_6): δ 3.37 (3 H, s, OCH_3), 3.68 (3 H, s, OCH_3), 3.72 (3 H, s, OCH_3), 3.77 (3 H, s, OCH_3), 6.56 (1 H, d, J=1.7 Hz, H-Ar), 6.70 (1 H, dd, J=1.7 and 8.1 Hz, H-Ar), 6.77 (1 H, d, J=1.7 Hz, H-Ar), 6.81 (1 H, dd, J=1.7 and 8.5 Hz, H-Ar), 6.85 (1 H, d, J=8.5 Hz, H-Ar), 6.99 (1 H, d, J=8.1 Hz, H-Ar), 7.67 (1 H, s, vinyl proton), 12.5 (1 H, br s, COOH). In a ^{13}C NMR experiment $^3J_{CH}$ for the coupling between the carbon in the carbonyl group and the vinyl proton was determined as 7.2 Hz. As expected[24] an examination of the *Z* isomer[25] gave a larger value (12.3 Hz) for the corresponding coupling constant.

(Z)-3,3′,4,4′-Tetramethoxystilbene was prepared by decarboxylation of **21** according to Battersby and Greenock.[26] Minor amounts of the *E*-isomer were present in the crude product. Recrystallization from ethanol gave a product melting at 120–121 °C (lit.[26] 117–118 °C). ^{1}H NMR spectrum: δ 3.68 (6 H, s, OCH_3), 3.87 (6 H, s,

OCH_3), 6.47 (2 H, s, vinyl protons), 6.77 (2 H, d, J= 8 Hz, H-Ar), 6.8–6.9 (4 H, m, H-Ar).

(E)-3,3',4,4'-Tetramethoxystilbene (**7**) was prepared by decarboxylation of (*Z*)-2,3-bis(3,4-dimethoxyphenyl)propenoic acid[25] following the procedure used for the preparation of the *Z* isomer (see above). Traces of the *Z* isomer were present in the crude product. Crystallization from ethanol gave a product melting at 155 °C (lit.[5] 157 °C). ^{1}H NMR data are given in Ref. 5.

threo-*1,2-Bis(3,4-dimethoxyphenyl)-1,3-propanediol* (**5b**) *and 2,3-bis(3,4-dimethoxyphenyl)-1,2-propanediol* (**22**). Borane–dimethyl sulfide complex (12 ml of a 2 M solution in tetrahydrofuran) was injected into a solution of acid **21** (2.75 g) in tetrahydrofuran (50 ml) (argon atmosphere). The reaction mixture was kept at 40 °C for 2.5 h. Excess reagent was decomposed by the addition of water (12 ml). H_2O_2 (1.6 ml 35% solution) and 3 M NaOH (16 ml) were added. The mixture was stirred vigorously for 1 h at 40 °C. The organic layer obtained after addition of water (50 ml) and subsequent extraction with chloroform (100 + 2 × 30 ml) was dried over Na_2SO_4. The oily residue obtained on removal of the solvents (film evaporation) was treated with methanol (30 ml) to decompose boric acid complexes;[27] the resulting product weighed 2.79 g. Flash chromatography [75 g SiO_2; eluents, dichloromethane–ethyl acetate (5:1) and (1:1)] gave a fraction (0.54 g) consisting primarily of **22** [2,3-bis(3,4-dimethoxyphenyl)-1-propanol was present as a contaminant] and a second fraction (1.44 g) consisting of **5b** and **22**. 1,3-Diol **5b** was purified from this latter fraction by reversed-phase chromatography [50 g Matrex (C8–60A-50um) (Amicon); eluent, acetone–water (2:5)]; the effluent fractions, pooled based on TLC examinations, were extracted with chloroform. Work-up of the extract gave crystals (1.11 g) melting at 124–125 °C (recrystallization from acetone did not change the m.p.). Yield: 40%. ^{1}H NMR (acetate derivative) and ^{13}C NMR spectra were in accordance with published NMR data[17] for **5b**. A fraction consisting of **22** (0.18 g) was also obtained from the reversed phase column. This fraction was combined with the fraction of **22** obtained from the normal phase column. Recrystallization from acetone gave **22** (0.43 g) of m.p. 111–113 °C. ^{1}H NMR spectrum of **22**: δ 1.90 (1 H, dd, J=4.6 and 8.2 Hz, prim. OH), 2.48 (1 H, s, tert. OH), 3.09 (2 H, s, CH_2Ar), 3.66 (3 H, s, OCH_3), 3.76 (1 H, dd, J=8.2 and 11.3 Hz, CH_2O), 3.83 (3 H, s, OCH_3), 3.84 (1 H, dd, J=4.6 and 11.3 Hz, CH_2O), 3.84 (3 H, s, OCH_3), 3.88 (3 H, s, OCH_3), 6.3–7.0 (6 H, m, H-Ar). ^{1}H NMR spectrum of the monoacetate of **22** (**23**): δ 2.05 (3 H, s, CH_3CO), 2.48 (1 H, s, tert. OH), 3.06 (2 H, AB spectrum, δ_A=3.09, δ_B=3.03, J=13.7 Hz, CH_2Ar), 3.66 (3 H, s, OCH_3), 3.83 (6 H, s, OCH_3), 3.88 (3 H, s, OCH_3), 4.36 (2 H, AB spectrum, δ_A=4.43, δ_B=4.29, J=11.7 Hz, CH_2O), 6.3–7.0 (6 H, m, H-Ar).

Methyl (E)-2,3-bis(3,4-dimethoxyphenyl)propenoate was prepared from **21** using the synthetic method applied for the preparation of methyl (*Z*)-2,3-bis(3,4-dimethoxyphenyl)propenoate.[25] M.p. 126–127 °C (from ethanol). ^{1}H NMR spectrum: δ 3.49 (3 H, s, OCH_3), 3.80 (3 H, s, OCH_3), 3.82 (3 H, s, OCH_3), 3.85 (3 H, s, OCH_3), 3.91 (3 H, s, OCH_3), 6.53 (1 H, d, J=2.0 Hz, H-Ar), 6.72 (1 H, d, J=8.4 Hz, H-Ar), 6.78 (1 H, d, J=2.0 Hz, H-Ar), 6.82 (2 H, dd, J=2.0 and 8.4 Hz, H-Ar), 6.92 (1 H, d, J=8.4 Hz, H-Ar), 7.77 (1 H, s, vinyl proton).

(E)-2,3-Bis(3,4-dimethoxyphenyl)-2-propen-1-ol (**8**)[13,14] was prepared by reduction of methyl (*E*)-2,3-bis(3,4-dimethoxyphenyl)propenoate with $LiAlH_4$ (cf. Gierer *et al.*[28]). Recrystallization from ethyl acetate gave a product melting at 113–114 °C (Lit.[14] 114–115 °C). Yield: 69%. ^{1}H NMR spectrum of the acetate derivative: δ 2.07 (3 H, s, CH_3CO), 3.53 (3 H, s, OCH_3), 3.77 (3 H, s, OCH_3), 3.82 (3 H, s, OCH_3), 3.88 (3 H, s, OCH_3), 4.89 (2 H, d, J=1.1 Hz, CH_2), 6.54 (1 H, br s, H-Ar), 6.60 [1 H, br s, vinyl proton (assigned on the basis of DEPT and HETCOR experiments)], 6.6–6.7 (2 H, m, H-Ar), 6.78 (1 H, d, J=1.8 Hz, H-Ar), 6.83 (1 H, dd, J=1.8 and 8.3 Hz, H-Ar), 6.87 (1 H, d, J=8.3 Hz, H-Ar).

(Z)-2,3-Bis(3,4-dimethoxyphenyl)-2-propen-1-ol[29] (**9**) was prepared by reduction of methyl (*Z*)-2,3-bis(3,4-dimethoxyphenyl)propenoate[25] using a method similar to that used for the synthesis-related compounds.[30] The starting material (1.07 g) was treated with $LiAlH_4$ (0.35 g) and $AlCl_3$ (0.42 g) in tetrahydrofuran for 20 h at 30 °C. The crude product (0.77 g) was crystallized from ethyl acetate giving a product (0.55 g) melting at 130–131 °C. Yield: 55%. ^{1}H NMR spectrum of the acetate derivative: δ 2.07 (3 H, s, CH_3CO), 3.90 (3 H, s, OCH_3), 3.92 (6 H, s, OCH_3), 3.94 (3 H, s, OCH_3), 5.16 (2 H, s, CH_2), 6.87–6.90 (4 H, m, H-Ar), 7.01 (1 H, s, vinyl proton), 7.0–7.1 (2 H, m, H-Ar). ^{13}C NMR spectrum of the acetate derivative: δ 21.1 (CH_3), 55.76 (OCH_3), 55.83 (OCH_3), 55.85 (OCH_3), 55.9 (OCH_3), 62.3 (CH_2), 109–150 [109.4, 111.00, 111.03, 111.9, 118.7, 121.6, 129.5, 133.2, 134.1, 148.5, 148.69, 148.76, 149.82; aromatic C and vinyl C (quaternary)], 132.3 (vinylic HC; assigned on the basis of DEPT and HETCOR experiments), 171.1 (CO).

1,2-Bis(3,4-dimethoxyphenyl)-1-propanone (**11**) was prepared by methylation of deoxyveratroin[31] according to a procedure used[1] in connection with the synthesis of 1,2-bis(4-hydroxy-3-methoxyphenyl)-1-propanone. M.p. 134–135 °C (from acetone). ^{1}H NMR spectrum of **11**: δ 1.51 (3 H, d, J=6.8 Hz, CH_3), 3.83 (3 H, s, OCH_3), 3.85 (3 H, s, OCH_3), 3.89 (3 H, s, OCH_3), 3.90 (3 H, s, OCH_3), 4.61 (1 H, q, J=6.8, >CH), 6.7–6.9 (4 H, m, H-Ar), 7.55 (1 H, d, J=2.0 Hz, H-Ar), 7.61 (1 H, dd, J=2.0 and 8.4 Hz, H-Ar).

2,3-Bis(3,4-dimethoxyphenyl)propanal (**14**). Compound **22** (157 mg) was refluxed with 20 ml 0.1 M HBr in

dioxane–water (9:1) for 30 min. Work-up (see 'acidolysis procedure') gave a product weighing 140 mg. Purification by flash chromatography [40 g SiO_2; eluents, dichloromethane–ethyl acetate (20:1) and (10:1)] gave **14** (111 mg) of m.p. 78–79 °C. ^{1}H NMR spectrum of **14**: δ 2.90 (1 H, dd, J=7.8 and 14.0 Hz, CH_2), 3.37 (1 H, dd, J=6.6 and 14.0 Hz, CH_2), 3.73 (1 H, m, >CH-), 3.76 (3 H, s, OCH_3), 3.83 (6 H, s, OCH_3), 3.87 (3 H, s, OCH_3), 6.5–6.9 (6 H, m, H-Ar), 9.73 (1 H, d, J= 1.5 Hz, CHO).

α-Chloromethyl-3,3',4,4'-tetramethoxystilbene (**18**) was prepared from **8** using the procedure described by Corey *et al.*[32] for the synthesis of (*Z*)-5-chloro-3-methyl-2-penten-1-ol. The crude product consisted of a mixture of the *Z* form (**18a**) and *E* form (**18b**) (^{1}H NMR). Crystals of the *Z* form (m.p. 131–133 °C) were obtained from dichloromethane–cyclohexane. The structure was established by X-ray crystallography.[33] ^{1}H NMR spectrum of the *Z* form (**18a**): δ 3.92 (3 H, s, OCH_3), 3.93 (3 H, s, OCH_3), 3.94 (3 H, s, OCH_3), 3.95 (3 H, s, OCH_3), 4.65 (2 H, s, CH_2), 6.8–7.2 (6 H, m, H-Ar), 6.94 (1 H, s, vinyl proton). ^{1}H NMR spectrum of the *E* form (**18b**): δ 3.52 (3 H, s, OCH_3), 3.78 (3 H, s, OCH_3), 3.82 (3 H, s, OCH_3), 3.89 (3 H, s, OCH_3), 4.44 (2 H, s, CH_2), 6.5–7.0 (7 H, m, H-Ar and vinyl proton). The structure was derived from ^{1}H NMR spectral comparisons with **8** (and **9**).

α-Bromomethyl-3,3',4,4'-tetramethoxystilbene (**17**) was prepared by a method analogous to that used for the preparation of **18**. A mixture of the *Z* form (**17a**) and *E* form (**17b**) was obtained (^{1}H NMR). ^{1}H NMR spectrum of the *Z* form (**17a**): δ 3.925 (3 H, s, OCH_3), 3.932 (3 H, s, OCH_3), 3.95 (3 H, s, OCH_3), 3.96 (3 H, s, OCH_3), 4.59 (2 H, s, CH_2), 6.91 (1 H, s, vinyl proton), 6.9–7.2 (6 H, m, H-Ar). ^{1}H NMR spectrum of the *E* form (**17b**): δ 3.52 (3 H, s, OCH_3), 3.80 (3 H, s, OCH_3), 3.83 (3 H, s, OCH_3), 3.90 (3 H, s, OCH_3), 4.39 (2 H, s, CH_2), 6.5–7.0 (7 H, m, H-Ar and vinyl proton). The structures were derived from ^{1}H NMR spectral comparisons with the *E* and *Z* forms of **18**.

Acidolysis procedure. A typical acidolysis experiment with 0.1 M acid (or 0.2 M acid) in dioxane–water (9:1) as the reagent was performed as follows. The substrate (ca. 150 mg) was refluxed with the acidolysis reagent (20 ml) for the desired period of time. The acidity of the cooled acidolysis mixture was reduced by addition of 4.5 ml 0.4 M $NaHCO_3$ (9 ml in experiments with 0.2 M acid). The reaction mixture was extracted with chloroform (20 + 3 × 10 ml). The extract was dried (Na_2SO_4) and solvents removed by film evaporation. The residue was dried *in vacuo* over P_2O_5 and KOH. For further experimental details, see Refs. 12 and 34. The reaction products were examined by ^{1}H NMR spectroscopy (before and after acetylation). Quantitative estimates were performed with hexamethylbenzene (signal at δ 2.23) and docosane [signals at δ 0.88 (CH_3) and 1.26 (CH_2); the latter signal was used in the estimates] as internal standards (cf. Ref. 12). ^{1}H NMR data for acidolysis products (or their acetate derivatives) of **5** are given in this paper (**8–14**, **17a**, **17b**, **18a**, **18b**, **20**) and in the literature (**7**,[5] **15**,[15] **16**[3,16]).

Acidolysis of **5a** *on a preparative scale.* The products obtained on acidolysis [0.2 M HBr, 200 ml dioxane–water (9:1)] of **5a** (4.88 g) for 3.5 h were dissolved in chloroform. Crystals of **15** precipitated (cf. Ref. 15). The crystals were filtered off and the residue obtained on evaporation of the solvent was chromatographed on silica gel (280 g) using dichloromethane–ethyl acetate (20:1) as the eluent. Fractions consisting of crystalline stilbene **7** and ketone **11** were obtained. Fractions consisting of 2,2-bis(3,4-dimethoxyphenyl)propanal (**12**) [m.p. 98–99 °C (from ether)] and 1,1-bis(3,4-dimethoxyphenyl)-2-propanone (**13**) [m.p. 109 °C (from ether)] could be obtained from the column. ^{1}H NMR spectrum of aldehyde **12**: δ 1.75 (3 H, s, CH_3), 3.79 (6 H, s, OCH_3), 3.89 (6 H, s, OCH_3), 6.66 (2 H, d, J=2.2 Hz, H-Ar), 6.75 (2 H, dd, J=2.2 and 8.3 Hz, H-Ar), 6.87 (2 H, d, J=8.3 Hz, H-Ar), 9.82 (1 H, s, CHO). ^{1}H NMR spectrum of ketone **13**: δ 2.26 (3 H, s, CH_3), 3.84 (6 H, s, OCH_3), 3.87 (6 H, s, OCH_3), 5.02 (1 H, s, >CH), 6.7–6.9 (6 H, m, H-Ar). Small amounts (<35 mg) of compound **20** [m.p. 198–200 °C (from acetone)] were obtained from the column. ^{1}H NMR spectrum of **20**: δ 3.75 (6 H, s, OCH_3), 3.86 (6 H, s, OCH_3), 3.88 (6 H, s, OCH_3), 3.96 (6 H, s, OCH_3), 4.17 (2 H, s, CH_2), 6.57 (2 H, s, H-Ar), 6.80 (2 H, d, J=8.3 Hz, H-Ar), 6.86 (2 H, d, J=15.9 Hz, vinyl protons), 6.93 (2 H, d, J= 1.7 Hz, H-Ar), 6.99 (2 H, d, J=1.7 and 8.3 Hz, H-Ar), 7.15 (2 H, s, H-Ar), 7.18 (2 H, d, J=15.9 Hz, vinyl protons). ^{13}C NMR spectrum of **20**: δ 35.6 (CH_2), 55.77 (2 C, OCH_3), 55.85 (2 C, OCH_3), 55.92 (2 C, OCH_3), 55.96 (2 C, OCH_3), 108–149 [108.4 (2 C), 108.8 (2 C), 111.2 (2 C), 113.1 (2 C), 119.5 (2 C), 124.2 (2 C), 128.5 (2 C), 128.7 (2 C), 130.70 (2 C), 130.74 (2 C), 147.6 (2 C), 148.6 (2 C), 148.7 (2 C), 149.0 (2 C)] (aromatic carbons and vinyl carbons). The molecular ion (*m/z* 612.2753, calc. for $C_{37}H_{40}O_8$: 612.2723) was the base peak in the mass spectrum [mass spectra (EI, 70 eV) were recorded with a ZabSpec instrument (VG Analytical, Fisons instrument)].

Isolation of the allyl alcohols **8–10** *as acetate derivatives from acidolysis products.* The product obtained on acidolysis [0.1 M HBr, 60 ml dioxane–water (9:1)] of **5a** (628 mg) for 5 min was acetylated by treatment with acetic anhydride–pyridine (1:1) for 24 h. The ether-soluble part of the acetylated product [bromides **17a** and **17b** in the acidolysis product were converted into pyridinium salts (not ether-soluble) in connection with the acetylation] was chromatographed (100 g SiO_2) using mixtures of dichloromethane and ethyl acetate (20:1, 2:1, 1:1, 1:2, 0:1) as eluents. The fraction (18 mg) obtained from the effluent 600–650 ml consisted of a

mixture of the acetates of **8** and **9** (major constituent) (^{1}H NMR). The fraction (52 mg) obtained from the effluent 650–840 ml consisted primarily of the acetate of **8** (^{1}H NMR) (minor amounts of the acetate of **9** was present in the fraction). The acetate of **10** was present (^{1}H NMR) as a minor constituent in the material obtained from the effluent 480–650 ml. To obtain this compound in a pure state, **8** (149 mg) was acidolysed for 0.5 h using CH_3SO_3H (0.2 M) as the catalyst. Essentially pure **10** (17 mg) was separated from the reaction product by flash chromatography (90 g SiO_2; eluents, mixtures of dichloromethane and ethyl acetate). The product was acetylated and the acetate purified by flash chromatography (20 g SiO_2; eluents, mixtures of dichloromethane and ethyl acetate). The acetate of **10** (9 mg) was obtained in a pure state (^{1}H NMR). ^{1}H NMR spectrum of the acetate of **10**: δ 2.12 (3 H, s CH_3CO), 3.83 (3 H, s, OCH_3), 3.847 (3 H, s, OCH_3), 3.850 (3 H, s, OCH_3), 3.855 (3 H, s, OCH_3), 5.34 [1 H, t (approximately), J= 1.2 Hz, vinyl proton], 5.46 (1 H, br s, vinyl proton), 6.69 (1 H, br s, >CHO], 6.76 (1 H, d, J=8.2 Hz, H-Ar), 6.80 (1 H, d, J=8.2 Hz, H-Ar), ≈6.9 (3 H, m, H-Ar), 6.96 (1 H, dd, J=1.8 and 8.2 Hz, H-Ar). ^{13}C NMR spectrum of the acetate of **10**: δ 21.3 (CH_3), 55.79 (OCH_3), 55.81 (OCH_3), 55.84 (OCH_3), 55.86 (OCH_3), 76.1 (>CHO), 110–150 (110.1, 110.77, 110.80, 110.9, 113.1, 119.3, 120.6, 130.6, 131.8, 146.8, 148.5, 148.7, 148.87, 148.94) (aromatic and vinyl carbons), 170.1 (CO).

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