Prins reaction in the synthesis of lignin model compounds III.* Alternative synthesis of pinoresinol, coniferyl aldehyde, and guaiacyl vinyl ketone

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A possibility to convert 4-aryl-5-bromo-1,3-dioxans, which are the products of Prins reaction on β-bromostyrenes, to the mixture of corresponding (E)-3-aryl-2-propene-1-ols and 1-aryl-2-propene-1-ols was demonstrated. This conversion, effected by zinc in wet *N*,*N*-dimethylformamide, allowed to prepare hitherto unknown 4-*O*-acetylconiferyl alcohol and 4-*O*-acetylguaiacylallyl alcohol, as well as their 5-bromo analogues, in the ratio about 5:1 and total yield over 85%. All four alcohols were oxidized to the corresponding carbonyl compounds subsequently deacetylated to give phenolic cinnamaldehydes and aryl vinyl ketones. Coniferyl and 5-bromoconiferyl alcohols obtained by deacetylation of their 4-*O*-acetates were oxidatively coupled to the corresponding resinols in yields of 40 and 58%, respectively. Although, debromination of 5,5′-dibromopinoresinol by catalytic hydrogenolysis of C—Br bonds gave high yields, application of bromine atom as a protective group in position 5 on the aromatic ring of coniferyl alcohol offered, therefore, little advantage. Mass spectral characteristics and ^{1}H-n.m.r. data of the compounds prepared are given.

Продемонстрирована возможность перевести 4-арил-5-бром-1,3-диоксаны, продукты реакции Принса β-бромстиролов, в смесь соответствующих (E)-3-арил-2-пропен-1-олов и 1-арил-2-пропен-1-олов при действии цинка в сыром диметилформамиде. Этим путем были приготовлены до сих пор неописанные 4-*O*-ацетилконифериловый спирт и 4-*O*-ацетилгваяцилаллиловый спирт или их 5-бромпроизводные, в отношении 5:1 и с выходом более 85%. Все четыре спирта были окислены на соответствующие карбонильные соединения, которые были впоследствии деацетилированы на фенольные циннамальдегиды и арилвинилкетоны. Конифериловый и 5-бромконифериловый спирты, которые были приготовлены деацетилированием 4-*O*-ацетилпроизводных подвергались дегидрогенации с образованием соответствующих резинолов с выходом 40 и 58% соответственно. Хотя реакция дебромирования 5,5′-дибромпинорезинола

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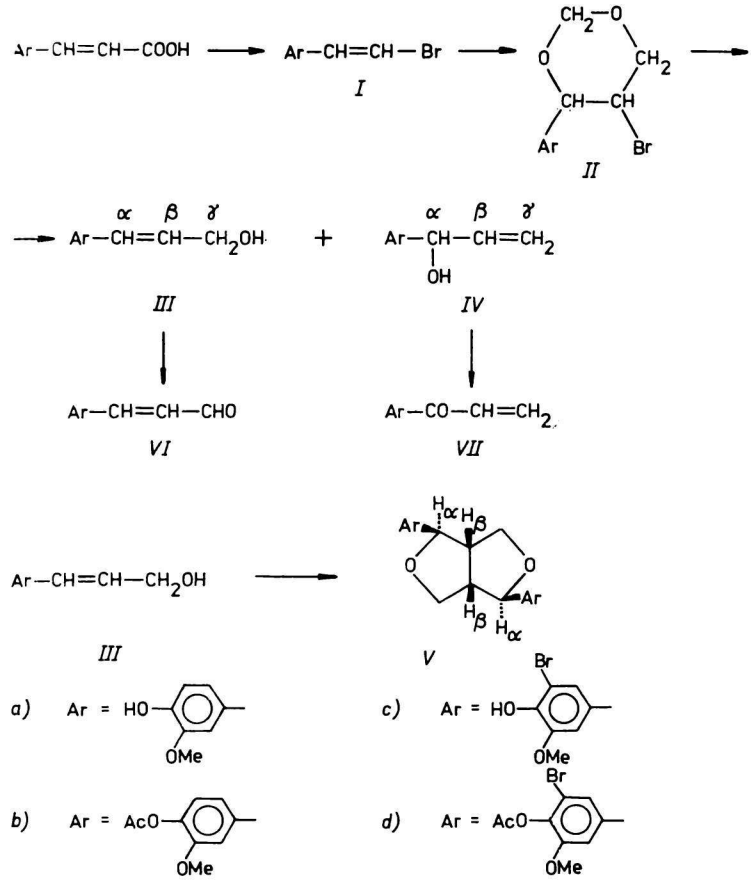
каталитическим гидрогенолизом связей C—Br дает хорошие выходы, апликация атома брома как протективной группы в положении 5 на ароматическом ядре конифферилового спирта приносит мало преимуществ. Приводятся ^{1}H-ЯМР и масс-спектры приготовленных соединений.

In the first part of this series we reported the preparation of two 4-aryl-5-bromo-1,3-dioxans, which were applied in a new synthetic route to 1-arylglycerols [1] from the corresponding β-bromostyrenes by means of Prins reaction. However, 4-aryl-5-bromo-1,3-dioxans appear to be useful synthetic intermediates also in some other model preparations of lignin. In this paper, we demonstrate two cases of their so far unknown transformation into isomeric couples of arylpropenols under the action of zinc powder. Thus, we prepared partially acetylated coniferyl alcohol and 1-guaiacylallyl alcohol, as well as their 5-bromo analogues, which are of value in preparation of the title lignin related compounds. We also evaluated the potential role of bromine atom as a protective group in position 5 on the aromatic ring in the synthesis of pinoresinol *via* oxidative coupling of coniferyl alcohol.

The halogen atom in 4-aryl-5-halo-1,3-dioxans was found rather unreactive in S_N reactions. This is, so far, the main obstacle which does not allow the application of these compounds in syntheses of arylglycerol β-aryl ethers as model substances representing the most characteristic interunit bond in lignin macromolecule. In our experiments, however, bromine atom in 4-aryl-5-bromo-1,3-dioxans was rather susceptible to eliminative action of metals. Thus, zinc in wet *N,N*-dimethylformamide converted the *trans*-arylbromodioxans *IIb, IId* (Scheme 1) to the corresponding (E)-3-aryl-2-propene-1-ols *IIIb, IIId* and 1-aryl-2-propene-1-ols *IVb, IVd* in the ratio of about 5 : 1 and high total yields (less selectively acted also other systems such as zinc in ethanol, acetic acid, active magnesium or sodium in ethers). This reaction reminds of the ring opening of 2-aryl-3-chlorotetrahydrofurans treated with sodium as described by *Normant* [2]. Position of olefinic bonds in the isomeric couples of arylpropenols was unequivocally established on the basis of their ^{1}H-n.m.r. spectra showing a distinct, two-proton doublet due to hydroxymethyl groups in *IIIb*, *IIId* and a two-proton double-doublet due to terminal methylene groups in *IVb*, *IVd*. Fragmentation reactions in mass spectrometer, characteristic of cinnamyl alcohols *IIIb* and *IIId*, included elimination of ketene from 4-*O*-acetyl groups (ionradicals $[M-42]^{+\cdot}$) and cleavage leading to the corresponding substituted benzaldehydes (ionradical peaks at *m/e* 152 and 232, 230, respectively). On the other hand, mass spectra of arylallyl alcohols *IVb* and *IVd* showed besides the ketene elimination also the production of benzylium ions as a result of fission of C—C (ion peaks at *m/e* 153 and 233, 231, respectively) or C—H bonds (ion peaks at *m/e* 179 and 259, 257, respectively).



Scheme 1

Protection of phenolic groups in 4-*O*-acetates *IIIb*, *IIId* and *IVb*, *IVd* allowed us to use manganese dioxide oxidation for the preparation of the corresponding aldehydes *VIb*, *VId* and ketones *VIIb*, *VIId*, respectively. Subsequent deacetylation yielded the phenolic *VIa* and *VIIa* usable as standards in lignin chemistry, since they were found to form during degradation of lignins and lignin model compounds [3—5]. It is of interest that mass spectra of cinnamaldehydes *VIb*—*VId* did not contain the strong peaks of ions $[M-1]^+$ reported to be characteristic of other cinnamaldehydes [6]. Explanation would probably require a more detailed study. Aryl vinyl ketones *VIIa*—*VIId* fragmented as expected [7], *i.e.* they largely produced aroyl ions with *m/e* 151 or 231, 229. This fragmentation pathway reliably distinguished them from the isomeric cinnamaldehydes.

Routine deacetylation of *IIIb* and *IIId* almost quantitatively yielded coniferyl (*IIIa*) and 5-bromoconiferyl alcohol (*IIIc*), which were directly used in the reaction of Fe(III) chloride catalyzed oxidative coupling in acetone—water 1:10 with the aim to prepare the corresponding resinols *Va* and *Vc*, respectively. Enzymic or transient metal salts catalyzed oxidative coupling of coniferyl alcohol is known to lead *via* intermediary resonance stabilized phenoxyl radical to simultaneous formation of the following three types of dimers: β-*O*-4 (guaiacylglycerol β-coniferyl ether), β-β (pinoresinol), and β-5 dimer (dehydrodiconiferyl alcohol) [8]. Relative amounts of individual dimers in the dehydrogenation product can be influenced to a certain extent by solvent polarity and/or arrangement of experiment. Namely, the β-β coupling was reported [8, 9] to be favoured at gradual addition of catalyst or enzyme to diluted solution of substrate in a highly polar solvent. Apart from exclusion of β-5 coupling, steric hindrance upon phenoxyl centre due to substitution in position 5 should be also a factor preferring β-β over β-*O*-4 coupling. However, *Tanahashi et al.* [9] more recently demonstrated in series of 3,5-disubstituted *p*-coumaryl alcohols (including three 5-substituted coniferyl alcohols) that in polar solvents electron-donating capability, represented by σ_p constants, rather than bulkiness of the substituent in position 5 correlated with the increasing ratio of β-β and β-*O*-4 dimers in dehydrogenation product.

Since in the above cited work of Tanahashi only relative amounts of β-β and β-*O*-4 dimers were determined from peak areas on ^{1}H-n.m.r. spectra, it was interesting to evaluate how the structural factors mentioned above would influence the preparative yield of the resinol in dehydrogenative coupling of 5-bromoconiferyl alcohol. Our comparison of dehydrogenation products of coniferyl and 5-bromoconiferyl alcohol showed that the latter gave just a little higher yield of β-β dimer (58%) than the former (40%) under the same conditions. This supports the explanation that exclusion of β-5 coupling and bulkiness of substituent in position 5,which are the factors justifying expectation of high prevalence of β-β dimer (resinol) in the product, are in 5-bromoconiferyl alcohol compensated by unfavourable electron-withdrawing effect of 5-bromo group ($\sigma_p = +0.23$; $\sigma_m = +0.39$). This, unfortunately, lowers the value of bromine atom as a protective group in position 5 in spite of the fact that the subsequent debromination of 5,5′-dibromopinoresinol was achieved smoothly by catalytic hydrogenolysis of C—Br bonds. Thus, we believe that preparation of pinoresinol *via* dibromopinoresinol is nearly equivalent in preparative value to dehydrogenation of unsubstituted coniferyl alcohol and both the methods are superior to other synthetic ways to pinoresinol [10—13].

The structures of resinols prepared (*Va—Vd*) were confirmed by mass spectra showing the presence of peaks analogous to those described for pinoresinol dimethyl ether [14]. For example, this was the case of ion and ionradical peaks produced from *Va* and *Vc* :$M^{+\cdot}$, $[M-30]^{+\cdot}$, peaks at *m/e* 180 and 260, 258; 163

and 243, 241; 152 and 232, 230; 151 and 231, 229; 137 and 217, 215, respectively. Relative pinoresinol configuration on tetrahydrofurofuran bicycle was confirmed by the presence of single spin coupling constant $J_{\alpha\beta}$ = 4.0—4.5 Hz on ^{1}H-n.m.r. spectra characteristic of cisoid spin interaction. Resinols of epipinoresinol configuration were not observed in the products.

Experimental

Melting points were determined on a Kofler hot-stage. The ^{1}H-n.m.r. spectra (80 MHz) were recorded with a Tesla BS 487 B spectrometer at 25°C with TMS as an internal standard. Proton signal assignments were made by the Indor technique. Mass spectra were measured with a JMS-100 D instrument at electron energy of 12 or 70 eV and an emission of 300 μA.

The reactions were monitored by thin-layer chromatography (t.l.c.) on Silica gel G (Merck). Spots were visualized by spraying the plates with 5% (v/w) sulfuric acid in ethanol and heating at 250°C. Preparative chromatography was carried out on columns of dry-packed Silica gel 60 (Merck) which prior to packing were equilibrated with 40% of the mobile phase.

The standard procedure of acetylation consisted in adding acetic anhydride (3—5 equivalents) to the solution of the substrate (1 g) in pyridine (30 ml) and allowing the mixture to stand overnight. Unreacted acetic anhydride was then decomposed by methanol and finally the solvents were removed by several evaporations with toluene at 50°C *in vacuo*.

The standard procedure of deacetylation consisted in addition of anhydrous potassium carbonate (1 equivalent) to the stirred solution of substrate (1 g) in methanol (80 ml) under the slight stream of nitrogen. Stirring was then continued for 2—5 h (t.l.c.), the mixture was deionized with a cation-exchange resin, filtered and concentrated at 40°C *in vacuo*.

Chloroform solutions were dried over sodium sulfate, partly decolorized with silica gel, filtered and concentrated at 40°C *in vacuo*.

(E)-5-Bromo-4-hydroxy-3-methoxystyryl bromide (Ic)

A solution of bromine (4 ml) in acetic acid (150 ml) was added dropwise to a stirred suspension of 5-bromoferulic acid [15] (22 g) in acetic acid (400 ml) at 15°C. The yellowish solution was then treated under the same conditions with anhydrous potassium acetate (24 g) and stirring was continued for 6 h at 20°C. The resulting mixture was concentrated to a small volume, chloroform was added (300 ml), inorganic salts were washed off by water and, after evaporation of chloroform, the product was crystallized from diluted acetic acid (11.6 g, 46%). Mother liquors were chromatographed on a short column in eluting system benzene—ethyl acetate 25:1 to give an additional crop of product (7.5 g, overall yield 77%). M.p. 87.5—88.5°C (recrystallized from heptane). For $C_9H_8O_2Br_2$ (308.0) calculated: 35.10% C, 2.62% H, 51.90% Br; found 35.28% C, 2.65% H, 51.66% Br. Mass spectral data (70 eV, 80°C): 310(53), 308(100), 306(53), 295(11), 293(22), 291(11), 267(3), 265(7), 263(3), 230(40), 228(40), 215(11), 213(13), 187(3), 185(4). ^{1}H-N.m.r. data

($CDCl_3$): 3.83 s, 3H (OMe); 6.02 bs, 1H (OH); 6.52 d, 1H (H_α); 6.60 d, 1H (H_{arom}); 6.75 d, 1H (H_β); 7.00 d, 1H (H_{arom}); $J_{\alpha\beta} = 13.5$ Hz.

trans-5-Bromo-4-(4-acetoxy-5-bromo-3-methoxyphenyl)-1,3-dioxan (IId)

Paraformaldehyde (3.5 g) and then boron trifluoride etherate (2 ml) were added to a stirred solution of the styryl bromide *Ic* (10 g) in dichloromethane (250 ml). T.l.c. showed completion of reaction after continued stirring for 2 h at 20°C. The reaction mixture was then diluted with chloroform, washed with saturated sodium hydrogen carbonate solution, water and processed in the usual manner. The residue was directly acetylated by the standard procedure. Crystallization from ethanol gave 12.0 g of crystalline product (90%) and column chromatography of mother liquors additional 0.5 g of product (totally 94%). M.p. 150.5—152°C (from ethanol). For $C_{13}H_{14}O_5Br_2$ (410.1) calculated: 38.07% C, 3.44% H, 38.98% Br; found: 38.11% C, 3.39% H, 38.01% Br. Mass spectral data (70 eV, 200°C): 412(2), 410(4), 408(2), 370(48), 368(100), 366(50), 310(1), 308(3), 306(1), 232(100), 230(100), 162(7), 150(7), 135(5), 108(12), 106(12), 94(12). ^{1}H-N.m.r. data ($CDCl_3$):2.33 s, 3H (OAc); 3.81 s, 3H (OMe); 3.70—4.50 m, 4H (CH_2); 4.80 d, 1H (H_α); 5.22 dd, 1H (H_β); $J_{\alpha\beta} = 6.0$ Hz.

(E)-3- and 1-(4-acetoxy-5-bromo-3-methoxyphenyl)-2-propene-1-ol (IIId and IVd)

Bromodioxan *IId* (4 g) and zinc powder (4 g) were suspended in *N, N*-dimethylformamide (80 ml) and after addition of water (8 ml) the mixture was vigorously stirred at 80°C for 3 h. After filtering off the unreacted zinc powder, the filtrate was diluted with water and extracted with chloroform several times. The combined extracts were washed with water and processed in the usual manner. The remains of *N,N*-dimethylformamide were removed by repeated codistillation with xylene at 55°C *in vacuo*. The resulting residue was partitioned on silica gel column with the mixture tetrachloromethane—acetone 7:1 as eluent.

IIId: yield 2.3 g (78.2%). For $C_{12}H_{13}O_4Br$ (301.1) calculated: 47.86% C, 4.35% H, 26.54% Br; found: 48.10% C, 4.31% H, 26.22% Br. Mass spectral data (70 eV, 185°C): 302(6), 300(6), 261(8), 260(90), 259(10), 258(90), 233(2), 232(26), 231(3), 230(28), 229(2), 217(40), 215(40), 204(20), 202(24), 150(34), 101(100). ^{1}H-N.m.r. data ($CDCl_3$): 2.33 s, 3H (OAc); 3.05 bs, 1H (OH); 3.75 s, 3H (OMe); 4.21 d, 2H (CH_2); 6.13 q, 1H (H_β); 6.44 d, 1H (H_α); 7.00 dd, 2H (H_{arom}); $J_{\alpha\beta} = 15.5$ Hz.

IVd: yield 0.34 g (11.6%). For $C_{12}H_{13}O_4Br$ (301.1) calculated: 47.86% C, 4.35% H, 26.54% Br; found: 48.02% C, 4.18% H, 26.39% Br. Mass spectral data (70 eV, 190°C): 302(6), 300(6), 261(12), 260(92), 259(16), 258(100), 257(6), 233(11), 231(17), 229(13), 227(10), 217(10), 215(10), 205(9), 204(10), 203(10), 202(11), 179(30), 124(47). ^{1}H-N.m.r. data ($CDCl_3$): 2.31 s, 3H (OAc); 3.14 s, 1H (OH); 3.75 s, 3H (OMe); 4.96 d, 1H (H_α); 5.16 q, 1H (CH_2); 5.91 o, 1H (H_β); $J_{\beta\gamma} = 15.5$ Hz.

(E)-3- and 1-(4-acetoxy-3-methoxyphenyl)-2-propene-1-ol (IIIb and IVb)

The compounds *IIIb* and *IVb* were prepared from *IIb* [1] in a quite analogous way as described above for *IIId* and *IVd*. Column chromatography was carried out using the mixture tetrachloromethane—acetone 6:1 as eluent.

IIIb: yield 76.6%. For $C_{12}H_{14}O_4$ (222.2) calculated: 64.85% C, 6.35% H; found: 65.03% C, 6.38% H. Mass spectral data (70 eV, 220°C): 222(27), 206(0.2), 194(0.4), 181(10), 180(100), 163(5), 152(18), 151(10), 137(8), 131(2), 124(5), 91(2). ^{1}H-N.m.r. data ($CDCl_3$): 2.31 s, 3H (OAc); 2.81 bs, 1H (OH); 3.04 d, 2H (CH_2); 3.80 s, 3H (OMe); 6.11 sextet, 1H (H_β); 6.55 d, 1H (H_α); 6.94 s, 3H (H_{arom}); $J_{\alpha\beta} = 15.5$ Hz.

IVb: yield 11.6%. For $C_{12}H_{14}O_4$ (222.2) calculated: 64.85% C, 6.35% H; found: 65.10% C, 6.41% H. Mass spectral data (70 eV, 210°C): 222(14), 205(1), 181(12), 180(100), 179(15), 165(4), 164(3), 163(15), 153(24), 151(26), 149(30), 137(30), 131(19), 125(50), 124(28). ^{1}H-N.m.r. data ($CDCl_3$): 2.30 s, 3H (OAc); 3.13 bs, 1H (OH); 3.75 s, 3H (OMe); 5.08 d, 1H (H_α); 5.18 q, 2H (CH_2); 6.95 m, 3H (H_{arom}); $J_{\alpha\beta} = 15.5$ Hz.

Dehydrogenative coupling of coniferyl (IIIa) and 5-bromoconiferyl alcohol (IIIc)

Methanolic solutions resulted from the standard deacetylation of *IIIb* or *IIId* (1.6 g) were concentrated after addition of few drops of *N,N*-dimethylformamide as a protection against traces of acids. The residue was dissolved in acetone (36 ml), water (360 ml) was added with stirring and then the solution of Fe(III) chloride hexahydrate in water (0.9 g in 4 ml) was added and stirring was continued at 20°C for 3 h. The mixture was extracted with chloroform and the extracts were processed as usual.

Va: Subsequent column chromatography with toluene—acetone 12:1 as eluting mixture yielded 0.52 g (40%) of *Va*. M.p. 118—120°C from diluted ethanol (Ref. [16] gives 121°C). Mass spectral data (12 eV, 100°C): 358(59), 328(6), 234(4), 206(9), 205(14), 194(22), 180(19), 163(100), 152(19), 151(88), 150(28), 149(22), 137(25), 131(88). ^{1}H-N.m.r. data ($CDCl_3$): 3.09 m, 2H (H_β); 3.85 dd, 2H ($H_{\gamma 1}$); 3.90 s, 6H (OMe); 4.23 dd, 2H ($H_{\gamma 2}$); 4.85 d, 2H (H_α); 4.95 s, 2H (OH); 7.00 m, 6H (H_{arom}); $J_{\alpha\beta} = 4.5$ Hz; $J_{\beta\gamma 1} = 4.0$ Hz; $J_{\beta\gamma 2} = 7.0$ Hz; $J_{gem} = 9.5$ Hz.

Va diacetate (*Vb*): M.p. 160—162°C (from ethanol; Ref. [10] gives 162—164°C). Mass spectral data (70 eV, 200°C): 442(22), 400(82), 358(88), 327(9), 250(6), 234(6), 221(9), 206(12), 205(22), 163(49), 152(35), 151(100), 150(37), 137(59). ^{1}H-N.m.r. data ($CDCl_3$): 2.31 s, 6H (OAc); 3.06 m, 2H (H_β); 3.90 dd, 2H ($H_{\gamma 1}$); 3.86 s, 6H (OMe); 4.27 dd, 2H ($H_{\gamma 2}$); 4.78 d, 2H (H_α); $J_{\alpha\beta} = 4.0$ Hz; $J_{\beta\gamma 1} = 3.5$ Hz; $J_{\beta\gamma 2} = 7.0$ Hz; $J_{gem} = 9.5$ Hz.

Vc: Crystallization from ethanol gave 0.20 g and subsequent column chromatography of mother liquors with tetrachloromethane—acetone 4:1 as elution mixture further 0.60 g of *Vc* (totally 58%). M.p. 202—205°C (from ethanol). For $C_{20}H_{20}O_6Br_2$ (516.2) calculated: 46.53% C, 3.91% H, 30.96% Br; found: 46.77% C, 3.99% H, 30.81% Br. Mass spectral data (70 eV, 240°C): 518(26), 516(51), 514(26), 488(2), 486(4), 484(2), 438(12), 437(11), 436(12), 435(9), 260(14), 258(18), 243(18), 241(18), 232(30), 231(82), 230(49),

229(79), 228(27), 217(55), 215(55), 162(100), 151(61). ^{1}H-N.m.r. data ($CDCl_3$): 3.69 m, 2H (H_β); 3.88 s, 6H (OMe); 4.24 m, 4H (CH_2); 4.68 d, 2H (H_α); 8.00 bs, 2H (OH); $J_{\alpha\beta}=4.0$ Hz; $J_{\beta\gamma_1}=3.5$ Hz; $J_{\beta\gamma_2}=7.5$ Hz; $J_{gem}=9$ Hz.

Vc diacetate (*Vd*): M.p. 204—206°C (from acetic acid). For $C_{24}H_{24}O_8Br_2$ (600.3) calculated: 48.02% C, 4.03% H, 26.63% Br; found: 47.95% C, 4.08% H, 26.37% Br. Mass spectral data (70 eV, 250°C): 602(1), 600(2), 598(1), 560(14), 558(26), 556(13), 518(30), 516(56), 514(30), 438(4), 437(5), 436(5), 435(4), 260(5), 258(10), 231(28), 229(28), 217(28), 215(28), 162(32). ^{1}H-N.m.r. data ($CDCl_3$): 2.35 s, 6H (OAc); 3.32 m, 2H (H_β); 3.88 s, 6H (OMe); 4.25 m, 4H (CH_2); 4.79 d, 2H (H_α); 7.19 s, 4H (H_{arom}); $J_{\alpha\beta}=4.0$ Hz; $J_{\beta\gamma_1}=3.5$ Hz; $J_{\beta\gamma_2}=7.0$ Hz; $J_{gem}=9$ Hz.

Dehalogenation of 5,5'-dibromopinoresinol (Vc)

Dibromopinoresinol (1 g) was dissolved in the mixture acetone—methanol 1:2 (45 ml) under heating. After cooling, palladium on charcoal (moisture 40%, 10% Pd/C, 1 g) and pyridine (0.3 ml) were added and the mixture was hydrogenated at almost atmospheric pressure for 48 h at 20°C. The catalyst was then removed by filtration on a layer of asbestos, the filtrate was concentrated and acetylated by the standard procedure. Crystallization from ethanol gave 0.53 g (62%) of pinoresinol diacetate (*Vb*). Remaining traces of di- and monobromo derivative were separated by chromatography with linear gradient elution using the mixtures toluene—acetone 20:1 and 10:1. Total yield 79%. Pinoresinol (*Va*) was recovered almost quantitatively by the standard deacetylation.

Oxidation of 3- and 1-arylpropenols IIIb, IIId and IVb, IVd

Individual arylpropenols were dissolved in chloroform (30 ml per 1 g of substrate) and treated with active manganese dioxide (10 equivalents, Ref. [17]) under stirring for 5—8 h, until t.l.c. showed the disappearance of the starting material. After removal of manganese salts on a layer of asbestos and thorough washing of the filtration cake, the filtrate was concentrated *in vacuo*, crystallized and/or purified by column chromatography.

Phenolic compounds *VIa*, *VIc* and *VIIa*, *VIIc* were prepared by the standard deacetylation of the corresponding acetates *VIb*, *VId*, and *VIIb*, *VIId*, respectively, in almost quantitative yield.

VIb: yield 86%. M.p. 101—103°C (from ethanol; Ref. [18] gives 102—103°C). Mass spectral data (12 eV, 70°C): 220(8), 178(100), 163(8), 161(10), 147(19), 135(12), 124(1), 118(1), 107(1). ^{1}H-N.m.r. data ($CDCl_3$): 2.35 s, 3H (OAc); 3.86 s, 3H (OMe); 6.65 dd, 1H (H_β); 7.13 m, 3H (H_{arom}); 7.43 d, 1H (H_α); 9.69 d, 1H (H_γ); $J_{\alpha\beta}=15.5$ Hz; $J_{\beta\gamma}=7.5$ Hz.

VId: yield 88%. M.p. 150—152°C (from ethanol). For $C_{12}H_{11}O_4Br$ (299.1) calculated: 48.18% C, 3.71% H, 26.72% Br; found: 47.98% C, 3.77% H, 26.55% Br. Mass spectral data (12 eV, 60°C): 300(5), 298(5), 258(100), 256(100), 243(2), 241(2), 230(4), 228(4), 227(4), 225(4), 215(4), 213(4), 177(37). ^{1}H-N.m.r. data ($CDCl_3$): 2.41 s, 3H (OAc); 3.91 s, 3H (OMe); 6.64 dd, 1H (H_β); 7.04 d, 1H (H_{arom}); 7.35 d, 1H (H_{arom}); 9.70 d, 1H (Hγ); $J_{\alpha\beta}=16$ Hz; $J_{\beta\gamma}=7.0$ Hz.

VIIb: yield 82% (after column chromatography with benzene—ethyl acetate 20:1 as eluent). M.p. 72—75°C (from ethanol without recrystallization). For $C_{12}H_{12}O_4$ (220.2) calculated: 65.44% C, 5.49% H; found: 65.81% C, 5.42% H. Mass spectral data (12 eV, 60°C): 220(9), 178(100), 152(6), 151(50), 150(6), 135(3), 124(3). ^{1}H-N.m.r. data ($CDCl_3$): 2.34 s, 3H (OAc); 3.90 s, 3H (OMe); 5.94 dd, 1H ($H_{\gamma cis}$); 6.45 dd, 1H ($H_{\gamma trans}$); 7.11 dd, 1H (H_β); 7.2—7.6 m, 3H (H_{arom}); $J_{\beta\gamma trans} = 17$ Hz; $J_{\beta\gamma cis} = 10.6$ Hz; $J_{gem} = 2$ Hz.

VIId: yield 82% (after column chromatography with benzene—ethyl acetate 25:1). M.p. 95—98°C (from ethanol without recrystallization). For $C_{12}H_{11}O_4Br$ (299.1) calculated: 48.18% C, 3.71% H, 26.72% Br; found 48.41% C, 3.82% H, 26.25% Br. Mass spectral data (12 eV, 60°C): 300(7), 298(7), 258(100), 256(100), 231(26), 229(25), 177(44). ^{1}H-N.m.r. data ($CDCl_3$): 2.40 s, 3H (OAc); 3.91 s, 3H (OMe); 5.88 dd, 1H ($H_{\gamma cis}$); 6.41 dd, 1H ($H_{\gamma trans}$); 7.09 dd, 1H (H_β); 7.72 d, 1H (H_{arom}); 7.48 d, 1H (H_{arom}); $J_{\beta\gamma trans} = 17$ Hz; $J_{\beta\gamma cis} = 10.5$ Hz; $J_{gem} = 2$ Hz.

VIa: Column chromatography was carried out with benzene—ethyl acetate 7:1 as eluent. M.p. 80—82°C (from benzene; Ref. [19] gives 80—81°C). Mass spectral data (12 eV, 120°C): 178(100), 177(17), 163(11), 161(14), 147(25), 135(23), 124(10), 107(15).

VIc: Column chromatography was carried out with benzene—ethyl acetate 8:1 as eluent. M.p. 138—139°C (from ethanol). For $C_{10}H_9O_3Br$ (257.1) calculated: 46.72% C, 3.53% H, 31.09% Br; found: 46.66% C, 3.48% H, 30.82% Br. Mass spectral data (12 eV, 120°C): 258(100), 256(100), 243(4), 241(4), 230(7), 228(7), 227(8), 225(8), 216(12), 214(12), 177(54), 145(8), 133(8).

VIIa: Column chromatography was carried out with benzene—ethyl acetate 8:1 as eluent. For $C_{10}H_{10}O_3$ (178.2) calculated: 67.40% C, 5.66% H; found: 67.64% C, 5.76% H. Mass spectral data (12 eV, 90°C): 178(100), 151(95), 150(1), 135(1), 123(1).

VIIc: Column chromatography was carried out with benzene—ethyl acetate 13:1 as eluent. For $C_{10}H_9O_3Br$ (257.1) calculated: 46.72% C, 3.53% H, 31.09% Br; found: 46.55% C, 3.49% H, 30.88% Br. Mass spectral data (12 eV, 90°C): 258(100), 256(100), 231(100), 229(100), 204(5), 202(5), 178(10), 150(6).

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References

1. Brežný, R. and Alföldi, J., *Chem. Zvesti 32,* 684 (1978).
2. Normant, H., *Chim. Ind.* (Milan) *63,* 509 (1950).
3. Karig, F. and Stahl, E., *Holzforschung 28,* 201 (1974).
4. Kratzl, K., Kisser, W., Gratzl, J., and Silbernagel, H., *Monatsh. Chem. 90,* 771 (1959).
5. Unpublished results.
6. Biemann, K., *Mass Spectrometry,* p. 210. McGraw-Hill, New York, 1962.
7. Kováčik, V., Mihálov, V., and Brežný, R., *Cellulose Chem. Technol. 14,* 233 (1980).
8. Freudenberg, K. and Neish, A. C., *Constitution and Biosynthesis of Lignin,* pp. 82—91. Springer Verlag, Berlin, 1968.

9. Tanahashi, M., Takeuchi, H., and Higuchi, T., *Wood Res. 61,* 44 (1976).
10. Freudenberg, K. and Rasenack, D., *Chem. Ber. 86,* 755 (1953).
11. Kratzl, K. and Miksche, G. E., *Monatsh. Chem. 94,* 434 (1963).
12. Ogiyama, K. and Kondo, T., *Mokuzai Gakkaishi 13,* 345 (1967); *Chem. Abstr. 68,* 88325*x* (1968).
13. Katayama, Y. and Fukuzumi, T., *Mokuzai Gakkaishi 24,* 664 (1978); *Chem. Abstr. 89,* 216993*m* (1978).
14. Pelter, A., *J. Chem. Soc. C1967,* 1376.
15. Whaley, W. M., Meadow, M., and Dean, W. L., *J. Org. Chem. 19,* 1022 (1954).
16. Freudenberg, K. and Dietrich, H., *Chem. Ber. 86,* 4 (1953).
17. Attenburrow, J., Cameron, A. F. B., Chapman, J. H., Evans, R. M., Hems, B. A., Jansen, A. B. A., and Walker, T., *J. Chem. Soc. 1952,* 1094.
18. Freudenberg, K. and Dillenburg, R., *Chem. Ber. 84,* 67 (1951).
19. Krutošíková, A., Surá, J., Stankovský, Š., Polčin, J., and Kováč, J., *Cellulose Chem. Technol. 9,* 51 (1975).

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