Lignin–Feruloyl Ester Cross-links in Grasses. Part 2.[1] Model Compound Syntheses

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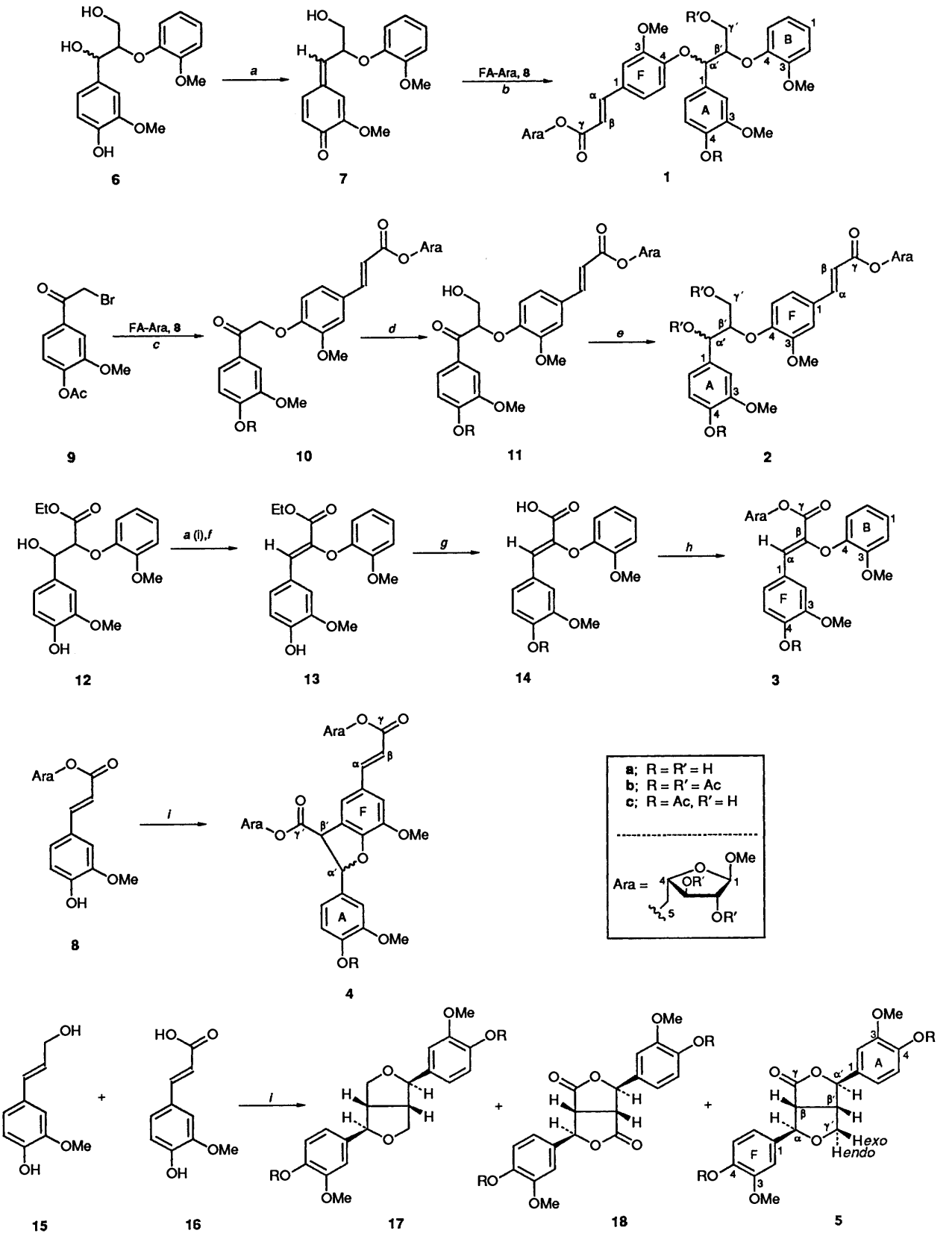
Five compounds which model the various structures produced when feruloyl esters are copolymerized into lignins have been synthesized. These models represent the lignin–feruloyl–polysaccharide structures which have been theorized to exist in the Graminaceae but have yet to be isolated. Complete spectroscopic characterization provides important chemical-shift information to facilitate the identification of these linkages in native lignins and synthetic DHP polymers. Methyl 5-*O*-{4-*O*-[3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propyl]feruloyl}-α-L-arabinofuranoside, a model for the α-linkage of feruloyl esters to lignin, was prepared as a mixture of *threo* and *erythro* isomers by addition of methyl 5-*O*-(*E*)-feruloyl-α-L-arabinofuranoside (FA-Ara) to the quinone methide derived from 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (guaiacylglycerol-β-guaiacyl ether). Methyl 5-*O*-{4-*O*-[2-hydroxy-2-(4-hydroxy-3-methoxyphenyl)-1-(hydroxymethyl)ethyl]feruloyl}-α-L-arabinofuranoside, a β-aryl ether model, was prepared by a method analogous to one used for the synthesis of guaiacylglycerol-β-guaiacyl ether; FA-Ara was added to 4-acetoxy-β-bromo-3-methoxyacetophenone, and the product was hydroxymethylated and reduced. The peracetate of methyl 5-*O*-[3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propenoyl]-α-L-arabinofuranoside, a compound which models the attack of lignin radicals on the β-position of the feruloyl ester, was prepared by elimination of the β-proton from the quinone methide derived from ethyl 3-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-propanoate. As in the preparation of synthetic copolymers between coniferyl alcohol and FA-Ara, only a single geometrical isomer was produced. Synthesis of both isomers of derived compounds and detailed NMR analysis indicated that this was the expected *Z*-isomer. A model for β-5 coupled products, 3-[3-carboxy-2-(4-hydroxy-3-methoxyphenyl)-7-methoxy-2,3-dihydrobenzofuran-5-yl]acrylic acid bis(methyl 5-deoxy-α-L-arabinofuranosid-5-yl) ester, was obtained as a *cis/trans* mixture in 55% yield by radical coupling of FA-Ara using silver(I) oxide. Finally, the crossed β-β compound 4,8-*exo*-bis(4-hydroxy-3-methoxyphenyl)-3,7-dioxabicyclo[3.3.0]octan-2-one (MEL) was obtained, in admixture with its isomer iso-MEL, pinoresinol, and the dilactone 4,8-*exo*-bis-(4-hydroxy-3-methoxyphenyl)-3,7-dioxabicyclo[3.3.0]octan-2,6-dione, from mixed radical coupling of coniferyl alcohol and ferulic acid *via* silver(I) oxide.

Ferulic acid [(*E*)-4-hydroxy-3-methoxycinnamic acid] in grasses is implicated in cross-linking cell-wall polysaccharides to lignins.[1] It has traditionally been assumed[2] that ether linkages to lignin were at the α-position (as modelled by compound 1, Scheme 1), implying attack of feruloyl esters on intermediate quinone methides produced during the free-radical coupling reactions involved in lignification. However, it has been demonstrated in model systems[1–3] that feruloyl esters will also become involved in the free-radical coupling process (as might be expected for any phenol). This leads, in addition to the occasionally mentioned[4–6] possibility of the β′-ether structure modelled by compound **2**, to three other structural types involving the β-position of the feruloyl moiety, structures modelled by compounds **3**–**5**. Considerable evidence has been found for each of these structural types in a synthetic lignin dehydrogenation polymer (DHP) of coniferyl alcohol **15** and methyl 5-*O*-(*E*)-[γ-^{13}C]feruloyl-α-L-arabinofuranoside **8** (9:1, respectively).[1]

This paper describes the syntheses and spectroscopic characterization of the model compounds **1**–**5** which were required for authentication of structures proposed in the DHP polymer. In some cases these syntheses represent expedient routes to the required compounds, but involve mixture separation. Although attempts have been made to use high-yielding and synthetically useful strategies, some reactions have not been carefully optimized. It is important to note, however, that compounds **1**–**4** accurately represent the cross-linking of α-L-arabinofuranosyl residues in arabinoxylans to lignin mediated by ferulic acid, and are the first reported compounds of this class.

Results and Discussion

Compound **1** (Scheme 1) is a model for the opportunistic,[3] or passive, incorporation of feruloyl esters into lignin. This type of structure is expected to arise in the polymer from simple nucleophilic addition of the phenol to an intermediate quinone methide (preceding paper,[1] Fig. 4). We chose to attach the feruloyl ester at the α-position of substrate **6** (Scheme 1), a model which represents the predominant β-*O*-4 interunit linkage of lignin.[7] The quinone methide **7** of guaiacylglycerol-β-guaiacyl ether [1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diol] **6** was generated, in methylene dichloride, by standard procedures,[8] and an excess of methyl 5-*O*-(*E*)-feruloyl-α-L-arabinofuranoside (FA-Ara) **8**[1,9,10] (2 mol equiv.) was added under basic conditions. Addition of a phenol to lignin model quinone methides is generally a low-yielding reaction in both organic and aqueous media.[11–13] We have found that the



Scheme 1 Synthetic schemes for compounds **1**–**5**. *Reagents and conditions: a*, (i) Me_3SiBr, CH_2Cl_2; (ii) $NaHCO_3$; *b*, DBU (0.07 mol equiv.); *c*, K_2CO_3, acetone, reflux; *d*, $H_2C{=}O$, 1,4-dioxane, K_2CO_3; *e*, $Zn(BH_4)_2$, EtOAc; *f*, DBU, CH_2Cl_2; *g*. (i) NaOH (aq.); (ii) Ac_2O, pyridine; *h*, (i) $SOCl_2$, PhH; (ii) methyl 2,3-di-*O*-acetyl-α-L-arabinofuranoside, pyridine; *i*, Ag_2O, acetone

use of an excess of phenol and a small amount of non-nucleophilic base {1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)} improves the yield and reproducibility of this type of addition. Our previous studies[14] with the addition of methyl ferulate or methyl *p*-coumarate to the quinone methide **7** indicated that the reaction yield was dependent upon the phenol, with methyl *p*-coumarate providing a higher yield (67% *vs.* 40%) as compared with methyl ferulate. The addition of the phenol **8** to the

Table 1 ^{1}H NMR data for the lignin–feruloyl ester cross-linked compounds[a]

Compound	α	β	α′	β′	γ′	A_f-5$_{pro-R}$	A_f-5$_{pro-S}$
threo-**1a**	7.571	6.405	5.608	4.533	3.702, 3.590	4.365	4.225
erythro-**1a**	7.580	6.421	5.569	4.566	3.934, 3.850	4.372	4.233
threo-**1b**	7.594	6.429	5.748	4.856	4.362, 4.136	4.505	4.318
erythro-**1b**	7.599	6.438	5.723	4.851	4.547, 4.444	4.507	4.320
threo-**2a**	7.633	6.466	4.90	4.400	3.733, 3.540	4.391	4.249
erythro-**2a**	7.612	6.442	4.90	4.472	3.833, 3.769	4.383	4.243
threo-**2b**	7.652	6.488	6.109	4.935	4.277, 4.062	4.526	4.336
erythro-**2b**	7.642	6.482	6.065	4.978	4.367, 4.252	4.525	4.337
3b	7.43					4.55	4.36
cis-**4a**[b]	7.667	6.475	6.033	4.496		4.383,[c] 4.378	4.219, 4.219
trans-**4a**[b]	7.667	6.471	6.011	4.496		4.386, 4.524	4.225, 4.313
5a	5.20	3.65	5.39	3.38	4.30$_{exo}$, 4.02$_{endo}$		
5b	5.29	3.72	5.52	3.45	4.39$_{exo}$, 4.12$_{endo}$		

[a] Values were determined in [$^2H_6$]acetone at 300 K with the central solvent peak as internal reference (δ 2.04). The numbering system is based on lignin nomenclature (see Scheme 1). [b] H/D exchanged prior to characterization. [c] The first set of A_f-5$_{pro-R/S}$-values corresponds to the A_f-5 protons of the C-γ linkage, the second set to those protons of the C-γ′ linkage.

quinone methide **7** gave a moderate yield (36%) of product **1a** as a mixture of isomers, the ratio depending on the reaction time. Silica gel chromatography provided enriched mixtures of *threo* (80%) and *erythro* (>95%) isomers. The free phenolic α-ethers are susceptible to α-cleavage, especially when in contact with an aqueous solvent.[14] Consequently these ethers were stored as their peracetylated derivatives.

As was found for the addition of methyl ferulate and *p*-coumarate,[14] the kinetic product was the *erythro* isomer. Longer exposure to the basic conditions led to equilibration, and eventually an approximately 50:50 mixture of stereoisomers of compound **1a** resulted. The stereochemistry of nucleophilic addition to quinone methides such as **7** has been extensively studied and, owing to the stability of the quinone methide (particularly when compared with the related carbonium ion), quite high stereoselectivity is generally observed. However, which isomer predominates depends on the nucleophile. For example, amines,[8] anthranol and anthrahydroquinone[15–17] all add to give predominantly the *threo* product, whereas acids[18] and phenols[11,12,14] give predominantly the *erythro* product. The *erythro* assignment in this case is from the characteristic chemical shifts of the upfield γ′-proton in the *threo* isomer (Table 1)—coupling constants are insufficiently different to be diagnostic.[14]

Compound **2**, the β′-feruloyl ether, models a structure with a fundamentally different mechanism of formation. No longer passive, but active incorporation of the feruloyl ester, *via* radical-coupling pathways, is the only way to obtain structures of this type in the lignin polymer.[3] The synthesis follows the classic route to the β-*O*-4 ethers[19,20] with the reaction modifications described previously.[14] Methyl 5-*O*-feruloyl-α-L-arabinofuranoside **8**[9] was added to 4-acetoxy-β-bromo-3-methoxyacetophenone **9** to afford the crystalline α-keto-β-(FA-Ara) compound **10c** in 78% yield. Subsequent hydroxyformylation in 1,4-dioxane–powdered K_2CO_3 gave compound **11c** in 82% yield. Reduction of the α-keto substituent with ethereal $Zn(BH_4)_2$[21,22] in ethyl acetate gave compound **2c** without cleavage of the A-ring 4-acetate. Portions of this material were then acetylated to give compound **2b**, or deacetylated ($NaHCO_3$ in MeOH–water, 50%)[23] to provide compound **2a**.

Our previous approach to the synthesis of model compounds **2** was *via* de-esterification of the methyl ester analogue of compound **2a**, which was prepared in an earlier study.[14] Acetylation and 1,3-dicyclohexylcarbodiimide (DCC)-mediated esterification with the methyl 2,3-di-*O*-acetyl-α-L-arabinofuranoside[9] afforded compound **2b**. Deacetylation to provide compound **2a** by using pyrrolidine in ethanol,[24] however, was not successful. The route utilizing addition of a large moiety **8** to the bromide **9** (a similar strategy to that used[20] in trimer syntheses) is much more versatile and should prove useful in providing other lignin–hydroxycinnamic acid–polysaccharide models.

Compound **3** represents the first of the radical-coupling products which involve the β-position of FA-Ara **8**. In the radical derived from the lignin monomer coniferyl alcohol **15**, the β-position is a predominant coupling site, and it was shown in the accompanying article[1] that β-position coupling is also favourable for the feruloyl ester FA-Ara **8**. We surmised that compound **3** would be most directly available, Scheme 1, from another β-ether lignin model precursor, ethyl 3-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propionate **12**, derived from the reported benzyl-protected compound.[25] Elimination of a β-proton from the quinone methide derived from compound **12** produced a single geometrical isomer of compound **13**. Subsequent saponification and acetylation gave acid **14b**, which was converted into the acid chloride ($SOCl_2$), and coupled with methyl 2,3-di-*O*-acetyl-α-L-arabinofuranoside in pyridine (67% from **14b**) to afford compound **3b**. Deacetylation was not attempted. Analogously, only a single isomer was detected in the DHP NMR spectra of the previous paper.[1] In order to assign the stereochemistry, both isomers of the benzylated derivative **19b** were prepared by treatment of the 4-*O*-benzyl-α-bromide derivative of compound **12** with DBU—the *E*1 mechanism *via* the carbonium ion was expected to be

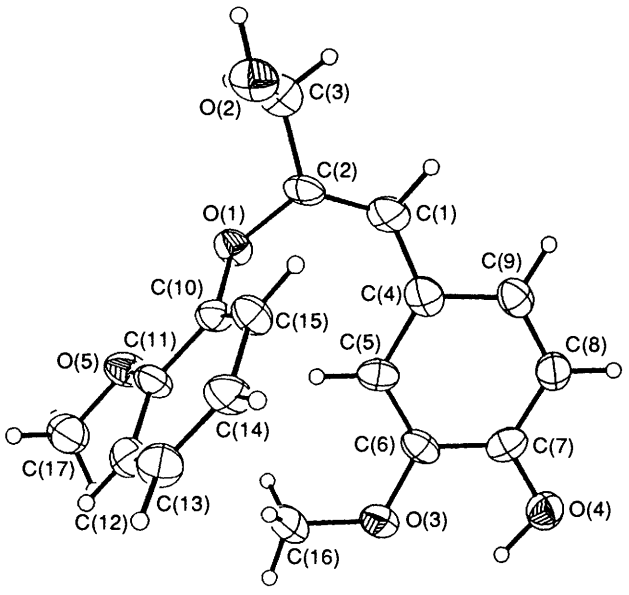
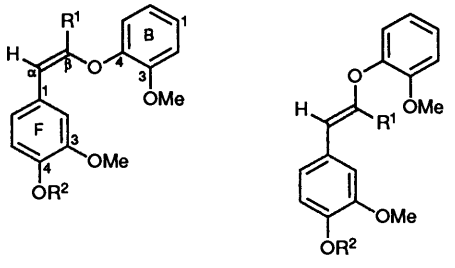


Fig. 1 X-Ray molecular structure of compound **19a**

less selective than elimination from the more stable quinone methide. Our assumption that the sole isomer of compound **13** produced from the quinone methide was the *Z*-isomer, an assumption made previously[26] for an analogous coniferaldehyde dimer, seems to be substantiated by $^3J_{C\gamma,H\alpha}$-values, but leads to some chemical-shift inconsistencies. Compounds **19d** or **19d-Ac** were sought as base compounds for the application of substituent effects. These compounds have previously been prepared from 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethanol (guaiacylglycol-β-guaiacyl ether) under extreme conditions in moderate yields.[27] High yields (97%) were obtained here by *in situ* preparation of the quinone methide from the α-bromide[8] and effecting the H_β elimination by using a strong non-nucleophilic base (DBU) at ambient temperature. The **19d** isomers are unambiguously assigned *Z* and *E* stereochemistry from the characteristic $J_{\alpha,\beta}$ coupling constants (*Z*, 6.8 Hz; *E*, 12.4 Hz). Application of substituent effects[28] for a CO_2R group to this base compound leads to predicted chemical shifts, Table 4, of δ_H 6.57 and 6.62 for (*Z*)-**13** and (*E*)-**13** [or (*Z*)-**19b** and (*E*)-**19b**], respectively. These very similar predicted chemical shifts do not reflect the observed differences between the two geometrical isomers of compound **19b**, prepared as a 60:40 *Z*:*E* mixture by treatment of the 4-*O*-benzyl-α-bromide derivative of compound **12** with DBU. Since the substituent effect tables[28] predict major differences for *Z* (1.01) *vs.* *E* (0.46) CO_2R, but only small substituent effects for *Z* (−0.01) *vs.* *E* (−0.02) CH_2O, we reduced compounds **19b** to produce compounds **19c** by using diisobutylaluminium hydride DIBAL-H.[29,30] Similarly, the assumed *Z*-isomer of compound **13**, obtained from the quinone methide reaction, was reduced with DIBAL-H to give compound **19a**, whose H_α chemical shift allowed isomer identification of the reduced products **19c**. The **19c** H_α chemical shifts, still widely divergent between *Z* (δ 6.21) and *E* (δ 5.62) isomers, were predicted in the reverse sense (δ 5.55 and 6.14, respectively) to our geometrical assignments. Using the data in Table 4, we calculate that *Z* and *E* substituent effects for CO_2Et are 1.79 and 0.30, and for CH_2OH are 0.65 and −0.54 respectively, at considerable variance with the standard parameters.[28] Since $^3J_{C,H}$ couplings follow typical Karplus behaviour similar to $^3J_{H,H}$,[31] and couplings of this type between a carbon and a *Z* or *E* proton on a double bond invariably have J_E (180° torsional angle) greater than J_Z (0° torsional angle), we wished to measure these values. Without resorting to selective pulse methods, long-range *J*-values were most readily determined from the reduced products **19c**—the esters **19b** had additional long-range coupling from C-γ to ethyl protons. Coupled DEPT^{++} experiments with a 45° editing pulse[32] gave the γ-CH_2OD carbon resonance as a triplet of doublets, the large-*J* (~142 Hz) triplet resulting from $^1J_{C\gamma,H\gamma}$ coupling, and the smaller doublet from $^3J_{C\gamma,H\alpha}$ coupling. In accord with Karplus behaviour, the $^3J_{C\gamma,H\alpha}$-values were 6.8 and 7.5 Hz for (*E*)-**19c** and (*E*)-**19c-Ac**, and 3.1 and 4.3 Hz for (*Z*)-**19c** and (*Z*)-**19c-Ac**. We therefore concluded that the sole isomer derived from the quinone methide was (*Z*)-**13**. Additional evidence for the assignment of *Z*- *vs.* *E*-isomers was gained from the ^{13}C NMR chemical shifts and NOE experiments. The C-γ chemical shift in (*Z*)-**19c** is higher than for (*E*)-**19c**, as expected for a CH_2OH group *Z* or *E* to H_α, respectively.[33] 1D NOE experiments showed a larger NOE to H_α when the H_γ protons of deuterium-exchanged (*Z*)-**19c** were irradiated than were observed when (*E*)-**19c** H_γ protons were irradiated (in a sample containing both isomers). Phase-sensitive 2D NOESY experiments provided more compelling evidence for the stereochemical assignment. A substantial NOE cross-peak for H_γ–H_α was observed in (*Z*)-**19c-Ac**, as well as a correlation between H_γ and the aromatic proton B-5. In (*E*)-**19c-Ac**, an extremely weak H_γ–H_α correlation was noted, along with major correlations between H_γ and aromatic protons F-2 and F-6. Clearly, then, the γ-CH_2OAc group is *Z* to the F-ring in the compound assigned as the *E*-isomer and *Z* to H_α in the *Z*-isomer. The *Z*-geometry of the styryl ether **13**, produced from the quinone methide, was firmly established from an X-ray structure of compound **19a** (derived from compound **13** by



Z-Isomer *E*-Isomer

13	$R^1 = CO_2Et$, $R^2 = H$
19a	$R^1 = CH_2OH$, $R^2 = H$
19b	$R^1 = CO_2Et$, $R^2 = CH_2Ph$
19c	$R^1 = CH_2OH$, $R^2 = CH_2Ph$
19c-Ac	$R^1 = CH_2OAc$, $R^2 = CH_2Ph$
19d	$R^1 = R^2 = H$
19d-Ac	$R^1 = H$, $R^2 = Ac$

Styryl ethers **13** and **19** prepared for isomer-identification of compounds **3**.

DIBAL-H reduction), Fig. 1 and Table 5. Interestingly, only the *Z*-isomer was detected in the DHP,[1] providing excellent evidence for β-proton elimination from a structurally analogous quinone methide. Finally, the *Z*-isomer of compound **19b** was shown to be thermodynamically preferred by isomerization with thiophenol[34]—a 40:60 *Z*:*E* mixture was converted into >95% (*Z*)-**19b** after 5 h (see Experimental section).

Compound **4** was prepared by mimicking the synthesis of analogous products in the polymer. We would have preferred a crossed dimer (combining coniferyl alcohol **15** and FA-Ara **8**) but the synthesis of compound **4** was more direct, and provided both a sufficiently good model for the phenylcoumaran structure and additional data for the remaining unsaturated moiety. FA-Ara **8** was subjected to one-electron oxidation using silver(I) oxide in acetone for 72 h, to give compound **4a** in 55% yield following purification. We had previously observed (unpublished) that Ag_2O oxidations in acetone produce

Table 2 ^{13}C NMR data for the lignin–feruloyl ester cross-linked compounds[a,b]

Carbon	*threo*-**1a**	*erythro*-**1a**	*threo*-**2a**	*erythro*-**2a**	*cis*-**4a**[c]	*trans*-**4a**[c]	**5a**
α	145.73	145.68	145.69	145.69	145.86	145.88	84.42
β	116.28	116.44	116.57	116.46	116.30	116.27	53.70
γ	167.23	167.23	167.29	167.29	167.29	167.29	177.71
α′	81.37	80.89	73.66	73.80	88.14	88.14	85.78
β′	86.61	85.45	87.11	85.62	55.95	55.89	50.37
γ′	61.87	61.61	61.91	61.96	170.92	170.92	73.43
A_f-1	110.38	110.38	110.36	110.36	110.38[d]	110.38,	
					110.45	110.43	
A_f-2	83.24	83.24	83.21	83.21	83.27,	83.27,	
					83.36	83.36	
A_f-3	79.32	79.32	79.28	79.28	79.28,	79.28,	
					79.28	79.47	
A_f-4	82.37	82.37	82.32	82.32	82.36,	82.36,	
					82.01	82.01	
A_f-5	64.85	64.85	64.90	64.90	64.80,	64.80,	
					65.65	66.19	
A-1	129.85	130.04	133.73	134.07	132.03	131.98	132.47
A-2	111.74	112.12	111.40	111.55	110.80	110.82	110.45
A-3	147.48	148.19	148.02	147.92	148.58	148.58	148.63
A-4	148.40	147.32	146.82	146.69	147.98	147.98	147.80
A-5	115.63	115.37	115.20	115.08	115.83	115.83	115.87
A-6	121.09	121.46	120.45	120.56	120.24	120.28	119.66
B-1	123.33	123.36					
B-2	113.55	113.59					
B-3	151.85	151.88					
B-4	149.94	149.13					
B-5	120.00	119.63					
B-6	121.96	121.80					
F-1	128.57	128.82	129.20	129.05	129.46	129.46	133.17
F-2	111.84	111.78	111.90	111.97	113.55	113.69	110.35
F-3	151.31	151.31	151.55	151.64	145.78	145.78	148.39
F-4	150.95	150.52	151.95	151.47	151.01	150.97	147.12
F-5	116.09	116.36	117.92	117.56	127.19	127.26	115.64
F-6	123.33	123.30	123.52	123.44	119.30	119.14	119.30

[a] Values were determined in [$^2H_6$]acetone at 300 K with the central solvent peak as internal reference (δ_C 29.80). [b] The numbering system is based on lignin nomenclature (see Scheme 1). [c] H/D exchanged prior to characterization. [d] The first set of A_f-values corresponds to the A_f carbons of the C-γ linkage, the second set to those of the C-γ′ linkage.

Table 3 ^{13}C NMR data for the lignin–feruloyl ester peracetates[a]

Carbon	*threo*-**1b**	*erythro*-**1b**	*threo*-**2b**	*erythro*-**2b**	**3b**	**5b**
α	145.70	145.70	145.65	145.61	126.73	84.01
β	116.69	116.75	116.85	116.95	140.82	53.59
γ	166.91	166.91	166.91	166.89	163.29	177.49
α′	81.09	80.69	75.20	74.36		84.93
β′	81.64	81.84	80.28	79.82		50.33
γ′	63.81	63.40	63.46	62.97		73.72
A_f-1	107.57	107.57	107.57	107.57	107.49	
A_f-2	82.11	82.11	82.11	82.11	82.02	
A_f-3	78.16	78.16	78.16	78.16	78.12	
A_f-4	81.33	81.33	81.34	81.34	81.14	
A_f-5	63.81	63.81	63.84	63.84	64.75	
A-1	136.89	137.29	136.40	136.37		139.95
A-2	112.65	112.61	112.63	112.82		111.05
A-3	152.23	152.16	152.22	152.08		152.62
A-4	140.80	140.68	140.94	140.83		140.96
A-5	123.50	123.36	123.58	123.34		123.96
A-6	120.26	120.35	120.31	120.50		118.53
B-1	123.64	123.87			123.78	
B-2	113.67	113.71			113.98	
B-3	151.86	151.99			150.00	
B-4	149.20	148.52			146.64	
B-5	119.32	119.86			114.89	
B-6	121.61	121.61			121.59	
F-1	129.22	129.29	129.86	130.07	132.25	140.68
F-2	112.00	112.00	112.23	112.31	114.62	110.86
F-3	151.45	151.45	151.70	151.88	152.23	152.38
F-4	150.45	150.35	151.18	150.44	141.95	140.40
F-5	116.53	116.58	117.96	118.40	123.89	123.65
F-6	123.20	123.20	123.21	123.14	124.27	118.40

[a] Refer to Table 2 and text for experimental details.

Table 4 Observed and predicted H_α chemical shifts, and $^3J_{C\gamma,H\alpha}$-values for styryl ethers **13** and **19a–d**

	Z-Isomer			*E*-Isomer		
Compound	H_α	$H_{\alpha pred}$	$^3J_{C\gamma,H\alpha}$	H_α	$H_{\alpha pred}$	$^3J_{C\gamma,H\alpha}$
13	7.34	(6.57)[a]			(6.62)[a]	
19a	6.19	(5.55)[b]			(6.14)[b]	
19b	7.35	(6.57)[a]		6.46	(6.62)[a]	
19c	6.21	(5.55)[b]	3.1	5.62	(6.14)[b]	6.8
19c-Ac	6.19	(5.62)[b]	4.3	5.81	(6.16)[b]	7.5
19d	5.56			6.16		
19d-Ac	5.63			6.18		

Z- and *E*-Isomers are as assigned from $^3J_{C\gamma,H\alpha}$ coupling constants and NOE data. ()[a]: predicted, from **19d**, using *cis*- and *trans*-CO_2R substituent effects of 1.01 and 0.46.[27] ()[b]: predicted, from **19d**, using *cis*- and *trans*-CH_2O substituent effects of −0.01 and −0.02.[27]

For these compounds, we find substituent effects of 1.79 and 0.30 for *cis*- and *trans*-CO_2Et, and 0.65 and −0.54 for *cis*-and *trans*-CH_2OH.

Table 5 Fractional atomic co-ordinates for compound **19a**[a]

	x	*y*	*z*
O(1)	0.3829(4)	0.3912(4)	0.3324(2)
O(2)	0.4369(4)	0.6055(5)	0.2137(2)
O(3)	0.1744(5)	0.3754(5)	0.5749(2)
O(4)	0.2417(5)	0.6171(5)	0.6548(2)
O(5)	0.2608(4)	0.1330(4)	0.3641(2)
C(1)	0.4645(6)	0.6254(7)	0.3855(3)
C(2)	0.4568(6)	0.5339(6)	0.3309(3)
C(3)	0.5418(6)	0.5632(7)	0.2674(3)
C(4)	0.4005(6)	0.6141(7)	0.4536(3)
C(5)	0.3140(6)	0.4909(7)	0.4791(3)
C(6)	0.2605(6)	0.4910(7)	0.5456(3)
C(7)	0.2911(6)	0.6157(7)	0.5884(3)
C(8)	0.3745(6)	0.7376(7)	0.5640(3)
C(9)	0.4296(7)	0.7371(7)	0.4983(3)
C(10)	0.2216(6)	0.3860(6)	0.3275(3)
C(11)	0.1588(6)	0.2436(6)	0.3444(3)
C(12)	−0.0014(6)	0.2257(7)	0.3403(3)
C(13)	−0.0927(7)	0.3453(7)	0.3188(3)
C(14)	−0.0294(6)	0.4862(7)	0.3027(3)
C(15)	0.1325(6)	0.5062(6)	0.3067(3)
C(16)	0.1521(9)	0.2397(8)	0.5352(3)
C(17)	0.1984(8)	−0.0150(7)	0.3817(4)

[a] Atom numbering is arbitrary, as on Fig. 1.

substantial amounts of phenylcoumaran products. Although a single spot on TLC, the ^1H and ^{13}C spectra of compound **4** indicated that both *cisoid* and *transoid* isomers were present. This is in contrast to the product resulting from analogous coupling of coniferyl alcohol radicals, which produces only the *transoid* isomer.[18,35] Attempts to separate these isomers have not been successful, and NMR (Tables 1–3) and MS (Experimental section) characterization has utilized the mixture. Owing to the extremely close ^{13}C and ^1H NMR chemical shifts of these two isomers (Tables 1–3) it is not possible to determine if both phenylcoumaran isomers were formed in the DHP.[1]

Compound **5**, which represents the coupling of both feruloyl ester and coniferyl alcohol radicals at their β-positions, is unique among the coupling products in that the arabinose moiety is lost in an internal transesterification. Compound **5** has recently been prepared[36] but the method is significantly more involved than we required in order simply to obtain material for authentication purposes. Consequently, compound **5** was prepared from oxidative coupling[37–39] of coniferyl alcohol **15** and ferulic acid **16**, again using Ag_2O as a one-electron oxidant. This oxidant, and the choice of acetone as solvent, allowed rapid formation of the desired products [30 min *vs.* 15–20 h with iron(III) chloride].[39] In addition to the expected and known symmetrical dimers **17** and **18**, the mixed dimer **5a** {4,8-*exo*-bis-(4-hydroxy-3-methoxyphenyl)-3,7-dioxabicyclo[3.3.0]octan-2-one} (monoepoxylignanolide, MEL) was obtained in low yield, together with its isomer {4-*endo*-8-*exo*-bis-(4-hydroxy-3-methoxyphenyl)-3,7-dioxabicyclo[3.3.0]octan-2-one} (isoMEL).[39] Attempted complete separation of this product mixture failed, but acetylation prior to isolation allowed purification of diacetate **5b**. Determination of the configuration of product **5** was supported by analysis of the ^1H–^1H spin–spin coupling constants whose values were in good agreement with those reported in the literature.[39] In addition, the ^1H spectrum of diacetate **5b** clearly revealed small couplings whose detection was improved by resolution enhancement. Their assignments were established *via* a long-range COSY experiment (Bruker's COSYLR pulse program, *d*6 = 225 ms, optimized for ~2 Hz couplings). Of particular note is the observation of a 32 peak pattern for the $H_{\beta'}$ signal indicating coupling to all protons in this dioxabicyclo[3.3.0]octane system (see Experimental section). In contrast, H_β is coupled only to $H_{\beta'}$, H_α, and $H_{\gamma'endo}$, and a weak correlation is observed with $H_{\alpha'}$ ($J < 0.5$ Hz) in the long-range COSY spectrum. The $H_{\gamma'endo}$ resonance showed correlations with four of the dioxabicyclo[3.3.0]octane derivative protons, lacking coupling with H_α, and $H_{\gamma'exo}$ correlated only with H_α, $H_{\beta'}$ and $H_{\gamma'endo}$. Similar analysis of the spin–spin-coupled proton network might be helpful for configurational determinations of isomeric dioxabicyclo[3.3.0]octane structures. A phase-sensitive NOESY experiment (Bruker's NOESYTP) further confirmed the stereochemistry of compound **5**. Strong correlations were observed between $H_{\beta'}$ and H_β, and between $H_{\beta'}$ and $H_{\gamma'exo}$. In addition to the intense cross-peak for $H_{\gamma'exo}/H_{\gamma'endo}$, the strong correlation of $H_{\gamma'endo}$ with $H_{\alpha'}$ confirmed the C-α′ configuration, whereas the weaker $H_{\gamma'endo}/H_\alpha$ and H_β/H_α correlations confirmed the configuration at C-α.

The NMR data, summarized in Tables 1 (^1H) and 2–3 (^{13}C), provide the necessary database for assignments of the long-range heteronuclear correlation spectra described in the preceding paper[1] and for attempts to find similar structures in isolated cell-wall materials. The A_f-5_{pro-R} and A_f-5_{pro-S} assignments are based on the D-pentofuranoside labelling studies of Wu *et al.*[40] The observed chemical shifts (A_f-$5_{pro-R} > A_f$-5_{pro-S}) and the coupling constants ($J_{4,5pro-R} < J_{4,5pro-S}$) are in accord with the values expected for L-pentofuranosides.[40–42] Assignments in the Tables were fully authenticated by use of the usual complement of 1D and 2D NMR techniques as described recently.[14] The inverse-detected long-range ^{13}C–^1H correlation experiment (HMBC) was particularly valuable in assigning shifts of aromatic ring carbons. The ^{13}C NMR chemical shifts of the α- and β-(FA-Ara) ethers (**1a**, **b** and **2a**, **b**) are in excellent agreement with the values of the analogous methyl esters,[14] the major differences being with the F-ring chemical shifts where differences were in the range of 0.02–0.25 ppm. The A- and B-ring differences were 0.00–0.04 ppm.

Experimental

General experimental aspects were as described in the previous paper.[1] NMR spectra of samples dissolved in [$^2H_6$]acetone at 300 K were run at 360 MHz on a Bruker AMX-360 spectrometer. Owing to problems associated with traditional acetylation [using (1:1) acetic anhydride–pyridine], small-scale acetylations (20 mg scale) were performed by dissolution of the starting material in CH_2Cl_2 (2 cm^3) and addition of acetic anhydride (50 mm^3, 5 mol equiv./OH group) followed by 4-(dimethylamino)pyridine (DMAP) (25 mg, 1.2 mol equiv./OH group). TLC indicated that the reaction was complete immediately but the reaction mixture was typically left for 1 h, at which time the mixture was quenched with absolute EtOH,

diluted with CH_2Cl_2, and washed successively with 3% HCl and water. Processing afforded the peracetylated materials in nearly quantitative yield.

Synthesis of Compounds 1

The synthesis of the α-ether trimers is based on the procedures recently described[14] for the methyl ester analogues.

Methyl 5-O-{4-O-[3-*Hydroxy*-1-(4-*hydroxy*-3-*methoxyphenyl*)-2-(2-*methoxyphenoxy*)*propyl*]*feruloyl*}-α-L-*arabinofuranoside* **1a**.—Compound **6**[43] (110.2 mg, 0.34 mmol) was converted into the quinone methide **7** in the usual way[8] (final solution volume ~ 30 cm^3). A solution of compound **8**[9] (226.3 mg, 0.66 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and DBU (4 mm^3, 0.078 mmol) were added. This solution was added dropwise to the stirred solution of quinone methide **7**, and once the addition was complete the mixture was left in the dark (*without* being stirred for 24 h. The yellow mixture was transferred to a separatory funnel and washed once with aq. NH_4Cl, dried over Na_2SO_4, and processed. Silica gel chromatography [silica (40 g); EtOAc–$CHCl_3$ (2:1; 400 cm^3); then EtOAc] gave compound **8** (116.4 mg, 51% unchanged), followed by the required compound **1a** (foam; 79.2 mg, 35.8%). Compound *erythro*-**1a** eluted first and could be obtained in >95% purity. The companion *threo* isomer was obtained in 80% purity along with an intermediate fraction that contained equal amounts of both isomers. Quenching of the reaction earlier than 24 h after commencement does not affect the reaction yield, but increases the proportion of the *erythro* isomer. DMAP-catalysed acetylation gave diacetate **1b** (Found: M^+, 810.2761. $C_{41}H_{46}O_{17}$ requires M, 810.2735).

Synthesis of Compounds 2

This synthesis follows a basic scheme used for preparation of lignin model dimers[19] and trimers.[20]

Methyl 5-O-{4-O-[2-(4-*Acetoxy*-3-*methoxyphenyl*)-2-*oxoethyl*]*feruloyl*}-α-L-*arabinofuranoside* **10c**.—Compound **9**[9] (140 mg, 0.49 mmol), FA-Ara **8**[9] (136 mg, 0.4 mmol) and K_2CO_3 (75 mg) were refluxed in acetone (10 cm^3). TLC [$CHCl_3$–EtOAc (1:1)] indicated that the disappearance of compound **8** was complete after 3 h. The mixture was filtered, and the filtrate was evaporated to give a syrup. Purification by silica gel chromatography afforded the *title compound* **10c** as a foam, which was crystallized from acetone–light petroleum (boiling range 40–60 °C) as needles (170 mg, 78%), m.p. 109.5–110.5 °C (Found: M^+, 546.1751. $C_{27}H_{30}O_{12}$ requires *M*, 546.1737); δ_H 4.25 (1 H, dd, *J* 6.3, 11.8, A_f-5_{pro-S}), 4.39 (1 H, dd, *J* 3.6, A_f-5_{pro-R}), 5.56 (1 H, s, β′-H), 6.47 (1 H, d, *J* 15.9, β-H) and 7.63 (1 H, d, α-H); δ_C 64.90 (A_f-5), 71.93 (C-β′), 110.38 (A_f-1), 116.55 (C-β), 145.65 (C-α), 167.25 (C-γ) and 193.72 (C-α′).

Methyl 5-O-{4-O-[2-(4-*Acetoxy*-3-*methoxyphenyl*)-1-(*hydroxymethyl*)-2-*oxoethyl*]*feruloyl*}-α-L-*arabinofuranoside* **11c**.—Compound **10c** (120 mg, 0.22 mmol) was dissolved in 1,4-dioxane (5 cm^3) and K_2CO_3 (245 mg) was added. Aq. formaldehyde (37% w/w; 35 mm^3, 0.47 mmol) was added and the mixture was stirred for 4 h at which time TLC (EtOAc) indicated that the reaction was complete. The inorganic salts were filtered off, and the filtrate evaporated to give a syrup, which was purified by silica gel chromatography (EtOAc) to afford the title compound **11c** as a foam (104 mg, 82%); δ_H 4.13 (2 H, m, γ′-H_2), 4.24 (1 H, dd, *J* 6.3, 11.8, A_f-5_{pro-S}), 4.38 (1 H, dd, *J* 11.8, 3.6, A_f-5_{pro-R}), 5.72 (1 H, t, *J* 4.8, β′-H), 6.45 (1 H, d, *J* 15.9, β-H) and 7.60 (1 H, d, α-H); δ_C 63.89 (C-γ′), 64.90 (A_f-5), 83.77 (C-β′), 110.38 (A_f-1), 116.83 (C-β), 145.47 (C-α), 167.19 (C-γ) and 196.18 (C-α′).

Methyl 5-O-{4-O-[2-(4-*Acetoxy*-3-*methoxyphenyl*)-2-*hydroxy*-1-(*hydroxymethyl*)*ethyl*]*feruloyl*}-α-L-*arabinofuranoside* **2c**.—Compound **11c** (82.3 mg, 0.14 mmol) was dissolved in EtOAc (2.5 cm^3) and cooled to 0 °C. Ethereal $Zn(BH_4)_2$[21] (~0.15 mol dm^{-3}; 2.3 cm^3) was added and the reaction was monitored by TLC [$CHCl_3$–MeOH (6:1)]. Complete conversion into a slower moving material was noted in 30 min. Excess of borohydride was quenched by the addition of water followed by HOAc. The solution was diluted with EtOAc and washed three times with saturated aq. NH_4Cl. Drying ($MgSO_4$) and processing gave compound **2c** as a 60:40 *threo*/*erythro* mixture (78.7 mg, 94%); δ_H *threo*: 4.244 (1 H, dd, *J* 11.8, 6.3, A_f-5_{pro-S}), 4.385 (1 H, dd, *J* 11.8, 3.6, A_f-5_{pro-R}), 4.46 (1 H, m, β′-H) and 5.02 (1 H, br d, *J* not clear, α′-H); *erythro*: 4.240 (1 H, dd, *J* 11.8, 6.3, A_f-5_{pro-S}), 4.380 (1 H, dd, *J* 11.8, 3.6, A_f-5_{pro-R}), 4.50 (1 H, m, β′-H) and 4.99 (1 H, br d, *J* not clear, α′-H); δ_C *threo*: 61.81 (C-γ′), 64.92 (A_f-5), 73.35 (C-α′), 86.50 (C-β′), 110.41 (A_f-1), 116.66 (C-β), 145.67 (C-α), 167.26 (C-γ) and 169.01 (OCOMe); *erythro*: 61.81 (C-γ′), 64.92 (A_f-5), 73.62 (C-α′), 85.45 (C-β′), 110.41 (A_f-1), 116.59 (C-β), 145.67 (C-α), 167.26 (C-γ) and 169.01 (OCOMe).

Methyl 5-O-{4-O-[2-*Hydroxy*-2-(4-*hydroxy*-3-*methoxyphenyl*)-1-(*hydroxymethyl*)*ethyl*]*feruloyl*}-α-L-*arabinofuranoside* **2a**.—Compound **2c** (51.4 mg) was dissolved in MeOH–water (1:1 v/v; 3 cm^3) and saturated aq. $NaHCO_3$ was added. The reaction mixture was stirred for 2 h to afford a mixture of four materials. The solution was filtered and the filtrate was diluted with EtOAc and washed twice with saturated aq. NH_4Cl. Subsequent processing and purification by preparative TLC (PLC) [$CHCl_3$–MeOH (6:1)] gave compound **2a** as a clear syrup (23.8 mg, 50%).

Peracetate **2b**. Compound **2c** (22 mg) was acetylated *via* the DMAP-catalysed method to afford *compound* **2b** in nearly quantitative yield (Found: M^+, 746.2419. $C_{36}H_{42}O_{17}$ requires *M*, 746.2422).

Synthesis of Compounds 3, and Styryl Ethers 13 and 19 required for Stereochemical Assignments

Compound **3** was prepared as a single geometrical isomer *via* a quinone methide derived from substrate **12**. In order to assign the stereochemistry (see text), related styryl ethers **19** were also synthesized.

Ethyl erythro-3-*Hydroxy*-3-(4-*hydroxy*-3-*methoxyphenyl*)-2-(2-*methoxyphenoxy*)*propanoate* **12**.—Debenzylation of Nakatsubo's β-ester[25] (*erythro*-isomer, 125 mg, 0.276 mmol) in ethanol (95%; 10 cm^3) was accomplished by using 5% Pd/C (12.5 mg) under hydrogen (balloon). A catalytic amount of acetic acid was added and the mixture was stirred for 3 h (monitoring by TLC). The Pd/C was filtered off, and the solvent was removed under reduced pressure to afford the title compound **12** (88 mg, 88%). Crystallization from CH_2Cl_2–light petroleum gave pure *erythro*-**12** as needles, m.p. 143.4–144.0 °C; δ_H 1.17 (3 H, t, *J* 7.1, *Me*CH_2O), 3.76 (3 H, s, F3-OMe), 3.84 (3 H, s, B3-OMe), 4.13 (2 H, q, *J* 7.1, MeCH_2O), 4.67 (1 H, d, *J* 6.6, β-H), 4.87 (br s, α-OH), 5.01 (1 H, br d, *J* 6.6, α-H) and 6.75–7.20 (7 H, ArH); δ_C(19 peaks) 74.58 (C-β), 83.59 (C-α) and 170.34 (C-γ).

Ethyl (Z)-3-(4-*Hydroxy*-3-*methoxyphenyl*)-2-(2-*methoxyphenoxy*)*propenoate* **13**.—Trimethylsilyl bromide (TMSBr, 213 mg, 1.390 mmol) was added to a stirred solution of compound **12** (252 mg, 0.70 mmol) in CH_2Cl_2 (10 cm^3). The mixture became pinkish indicating formation of the α-bromide derivative. After the mixture had been stirred for 30 min, DBU (265 mg, 1.741 mmol) was added for *in situ* generation of the quinone methide, followed by β-proton elimination. The mixture became

yellow and was stirred for 30 min. The solution was then diluted in CH_2Cl_2 (50 cm^3) and washed successively with 1 mol dm^{-3} hydrochloric acid, water, and saturated aq. NaCl. The organic layer was dried over sodium sulfate and evaporated to dryness to afford a single geometrical isomer (*Z*)-**13** in quantitative yield as a clear syrup; δ_H 1.18 (3 H, t, *J* 7.1, *Me*CH_2O), 3.71 (3 H, s, F3-OMe), 3.89 (3 H, s, B3-OMe), 4.18 (2 H, q, *J* 7.1, MeCH_2O), 6.75 (1 H, dd, *J* 8.0, 1.8, B-5), 6.80 (1 H, ddd, *J* 8.0, 7.2, 1.5, B-6), 6.84 (1 H, d, *J* 8.2, F-5), 6.95 (1 H, ddd, *J* 8.1, 7.2, 1.8, B-1), 7.05 (1 H, dd, *J* 8.1, 1.5, B-2), 7.23 (1 H, dd, *J* 8.2, 2.0, F-6), 7.34 (1 H, s, α-H), 7.51 (1 H, d, *J* 2.0, F-2) and 8.17 (br s, ArOH); δ_C(19 peaks) 14.43 (*Me*CH_2O), 55.87 (F3-OMe), 56.36 (B3-OMe), 61.53 (MeCH_2O), 127.57 (C-α), 138.82 (C-β), 164.03 (C-γ), 113.82 and 113.84 (F-2 and B-2), 114.40 (B-5), 115.92 (F-5), 121.48 (B-6), 123.31 (B-1), 125.41 (F-1), 125.85 (F-6), 146.95 (B-4), 148.23 (F-3), 149.31 (F-4) and 149.96 (B-3).

(Z)-3-(4-*Acetoxy*-3-*methoxyphenyl*)-2-(2-*methoxyphenoxy*)-*propenoic Acid* **14b**.—Compound (*Z*)-**13** was dissolved in 1,4-dioxane (3 cm^3) and hydrolysed with 2.5 mol dm^{-3} sodium hydroxide at ambient temperature overnight. The mixture was quenched with 1 mol dm^{-3} hydrochloric acid and extracted with ethyl acetate. The organic layer was washed, dried (Na_2SO_4), and evaporated. The residue was acetylated using standard procedure and work-up, and purified by silica gel chromatography [EtOAc–AcOH (200:1)] to yield the acid (*Z*)-**14b** (138 mg, 67%) as crystals, m.p. 169.6–170.7 °C; δ_H 2.21 (3 H, s, OAc), 3.70 (3 H, s, F3-OMe), 3.88 (3 H, s, B3-OMe), 6.81 (2 H, m, B-5 and B-6), 6.97 (1 H, m, B-1), 7.05 (1 H, d, *J* 8.2, F-5), 7.06 (1 H, m, B2), 7.35 (1 H, dd, *J* 8.3, 1.9, F-6), 7.42 (1 H, s, α-H) and 7.63 (1 H, d, *J* 1.9, F-2); δ_C(19 peaks) 20.40 (OCO*Me*), 55.90 (F3-OMe), 56.28 (B3-OMe), 113.78 (B-2), 114.52 (F-2), 114.56 (B-5), 121.49 (B-6), 123.52 (B-1), 123.79 (F-5), 124.09 (F-6), 126.46 (C-α), 132.41 (F-1), 141.16 (C-β), 141.71 (F-4), 146.72 (B-4), 149.90 (B-3), 152.11 (F-3), 164.45 (C-γ) and 168.83 (O*C*OMe).

Methyl 2,3-*Di*-O-*acetyl*-5-O-[(Z)-3-(4-*acetoxy*-3-*methoxyphenyl*)-2-(2-*methoxyphenoxy*)*propenoyl*]-α-L-*arabinofuranoside* **3b**.—Compound (*Z*)-**14b** (106.7 mg, 0.3 mmol) was mixed with benzene (5 cm^3) and thionyl dichloride (0.35 cm^3) and the mixture was refluxed for 45 min. The solution was evaporated to a syrup, which was diluted with toluene (distilled from CaH_2), and evaporated to give a syrup again. The syrup was dissolved in toluene (5 cm^3) and added *via* a dropping funnel to a solution of methyl 2,3-di-*O*-acetyl-α-L-arabinofuranoside (94.2 mg, 0.38 mmol) in pyridine (distilled from KOH; 1.8 cm^3). The reaction mixture was left for 2 h and was subsequently diluted with toluene and evaporated to give a syrup. The syrup was dissolved in CH_2Cl_2 and washed successively with water, cold 3% HCl, and water. Processing and subsequent silica gel chromatography [silica (40 g) in $CHCl_3$–EtOAc (19:1)] afforded *compound* (Z)-**3b** as a foam (110.7 mg, 63%) (Found: M^+, 588.1832. $C_{29}H_{32}O_{13}$ requires *M*, 588.1843); δ_H 2.04 and 2.05 (each 3 H, s, 2 × OAc), 2.21 (3 H, s, OAc), 3.32 (3 H, s, A_f-1-OMe), 3.71 (3 H, s, F3-OMe), 3.89 (3 H, s, B3-OMe), 4.22 (1 H, td, *J* 5.2, 3.6, A_f-4), 4.36 (1 H, dd, *J* 11.8, 5.4, A_f-5_{pro-S}), 4.55 (1 H, dd, *J* 11.8, 3.6, A_f-5_{pro-R}), 4.91 (1 H, br d, *J* 0.5, A_f-1), 5.02 (1 H, dd, *J* 1.7, 0.5, A_f-2), 5.03 (1 H, ddd, *J* 5.0, 1.7, 0.7, A_f-3), 6.82 (2 H, m, B-5 and B-6), 6.98 (1 H, m, B-1), 7.06 (1 H, d, *J* 8.2, F-5), 7.08 (1 H, dt, *J* 7.9, 0.9, B-2), 7.35 (1 H, dd, *J* 8.2, 1.9, F-6), 7.43 (1 H, s, α-H) and 7.62 (1 H, d, *J* 1.9, F-2).

β-(2-*Methoxyphenoxy*)*coniferyl Alcohol* (Z)-**19a**.—Compound (*Z*)-**13** (109 mg, 0.316 mmol) was dissolved in dry toluene (10 cm^3; distilled over CaH_2) and cooled in an ice–water-bath. DIBAL-H (0.9 cm^3 of a 1.5 mol dm^{-3} solution, 1.35 mmol) in toluene was added *via* syringe. Upon hydride addition, the mixture became yellow, then clear, indicating that the reaction was complete. Following quenching with ethanol and partial removal of solvents under reduced pressure, the mixture was extracted with EtOAc and the extract was successively washed with 0.1 mol dm^{-3} HCl, water, and saturated aq. NaCl. The organic layer was dried over Na_2SO_4 and evaporated to dryness to yield *compound* (Z)-**19a** (87 mg, 91%) as a yellow oil (Found: M^+, 302.1160. $C_{17}H_{18}O_5$ requires *M*, 302.1154). Crystallization from CH_2Cl_2–light petroleum gave pale yellow needles, m.p. 129.4–129.6 °C; δ_H 3.66 (3 H, s, F3-OMe), 3.86 (3 H, s, B3-OMe), 4.12 (2 H, br d, *J* 5.4, CH_2OH), 4.17 (1 H, dd, *J* 7.1, 4.6, CH_2OH), 6.19 (1 H, s, α-H), 6.70 (1 H, d, *J* 8.2, F-5), 6.80 (1 H, m, B-6), 6.93–7.05 (4 H, m, B-1, -2, -5 and F-6), 7.30 (1 H, d, *J* 1.9, F-2) and 7.51 (1 H, s, ArO*H*); δ_C(17 peaks) 55.80 (F3-OMe), 56.20 (B3-OMe), 61.91 (C-γ), 112.55 (F-2), 113.59 (B-2), 114.17 (C-α), 115.47 (F-5), 116.71 (B-5), 121.57 (B-6), 122.95 (F-6), 123.57 (B-1), 127.64 (F-1), 145.83 (B-4), 146.52 (F-4), 147.87 (F-3), 150.84 (B-3) and 151.00 (C-β); X-ray crystal structure—see below.

Ethyl 4-O-*Benzyl*-β-(2-*methoxyphenoxy*)*ferulate* **19b**.—β-Proton elimination of Nakatsubo's β-ester[25] (*erythro* isomer; 99 mg, 0.218 mmol) in CH_2Cl_2 (2 cm^3) was accomplished by using the same procedure as for compound **13** [TMSBr (67 mg, 0.437 mmol), DBU (99.6 mg, 0.654 mmol)] to afford the title compound **19b** (92.5 mg, 98%) as a 60:40 (but dependent on reaction time) *Z*:*E* isomeric mixture (yellow oil); (*Z*)-**19b** δ_H 7.35 (α-H); δ_C 127.21 (C-α), 139.36 (C-β) and 163.91 (C-γ); (*E*)-**19b** δ_H 6.46 (α-H); δ_C 121.68 (C-α), 143.81 (C-β) and 164.06 (C-γ).

Equilibration of Z/E-**19b**.—A sample of *Z*/*E*-**19b** enriched in the *E*-isomer (~40:60 *Z*:*E*; 11 mg, 0.025 mmol) was refluxed with thiophenol[34] (0.54 mg, 0.005 mmol) in toluene (2 cm^3) for 5 h. After removal of solvent, ^1H NMR analysis showed almost complete conversion (>95%) into the *Z*-isomer.

4-O-*Benzyl*-β-(2-*methoxyphenoxy*)*coniferyl Alcohol* **19c**.—By use of the same DIBAL-H method that produced compound **19a** from compound **13**, compounds **19b** (48.5 mg, 0.112 mmol) were reduced to afford the corresponding alcohols **19c** (38.5 mg, 88%). This 60:40 *Z*:*E* isomeric mixture was separated by PLC [chloroform–ethyl acetate (10:1)] to afford *compound* (Z)-**19c** (15 mg) and *compound* (E)-**19c** (15 mg) as clear syrups; for (*Z*)-**19c** (Found: M^+, 392.1617. $C_{24}H_{24}O_5$ requires *M*, 392.1624); δ_H 3.66 (3 H, s, F3-OMe), 3.86 (3 H, s, B3-OMe), 4.12 (2 H, br d, *J* 5.7, CH_2OH), 4.19 (1 H, dd, *J* 6.7, 5.2, CH_2OH), 5.06 (2 H, s, ArCH_2O), 6.21 (1 H, s, α-H), 6.80 (1 H, m, B-6), 6.89 (1 H, d, *J* 8.4, F-5), 6.94–6.99 (2 H, m, B-5 and B-1), 7.03 (1 H, dd, *J* 8.4, 2.0, F-6), 7.04 (1 H, m, B-2), 7.28 (1 H, m, Bn-4), 7.33 (1 H, d, *J* 2.0, F-2), 7.35 (2 H, m, Bn-3/5) and 7.44 (2 H, m, Bn-2/6); δ_C(22 peaks) 55.78 (F3-OMe), 56.24 (B3-OMe), 61.84 ($^3J_{C\gamma,H\alpha}$ 3.1, C-γ), 71.30 (ArCH_2O), 113.31 (F-2), 113.61 (C-α), 113.68 (B-2), 114.69 (F-5), 116.94 (B-5), 121.60 (B-6), 122.36 (F-6), 123.74 (B-1), 128.43 (Bn-2/6), 128.50 (Bn-4), 129.15 (Bn-3/5), 129.38 (F-1), 138.59 (Bn-1), 145.85 (B-4), 148.34 (F-4), 150.40 (F-3), 151.01 (B-3) and 151.96 (C-β); for (*E*)-**19c** (Found: M^+, 392.1619); δ_H 3.79 (3 H, s, F3-OMe), 3.83 (3 H, s, B3-OMe), 4.18 (1 H, t, *J* 5.7, CH_2OH), 4.35 (2 H, d, *J* 5.7, CH_2OH), 5.08 (2 H, s, ArCH_2O), 5.62 (1 H, s, α-H), 6.79 (1 H, dd, *J* 8.2, 2.1, F-6), 6.93–6.99 (3 H, m, F-2 and B-5, and B-6), 7.09–7.17 (3 H, m, B-1, B-2, and B-5), 7.29 (1 H, m, Bn-4), 7.36 (2 H, m, Bn-3/5) and 7.47 (2 H, m, Bn-2/6); δ_C(22 peaks) 56.11 (F3-OMe), 56.32 (B3-OMe), 60.06 ($^3J_{C\gamma,H\alpha}$ 6.8, C-γ), 71.47 (ArCH_2O), 109.57 (C-α), 113.74 (F-2), 114.32 (B-2), 115.08 (F-5), 121.65 (F-6), 121.90 (B-6), 123.07 (B-5), 125.99 (B-1), 128.43 (Bn-2/6), 128.50 (Bn-4), 129.16 (Bn-3/5), 130.28 (F-1), 138.64 (Bn-1), 145.07 (B-4), 148.02 (F-4), 150.62 (F-3), 152.69 (B-3) and 157.67 (C-β).

Acetylation in CH_2Cl_2 with Ac_2O–DMAP gave the acetates

19c-Ac in essentially quantitative yield, as clear oils; for (*Z*)-**19c-Ac** δ_H 1.95 (3 H, s, OAc), 3.68 (3 H, s, F3-OMe), 3.86 (3 H, s, B3-OMe), 4.65 (2 H, s, CH_2OAc), 5.08 (2 H, s, $ArCH_2O$), 6.19 (1 H, s, α-H), 6.84 (1 H, ddd, *J* 8.0, 7.3, 1.6, B-6), 6.93 (1 H, d, *J* 8.4, F-5), 6.99 (1 H, dd, *J* 8.0, 1.6, B-5), 7.02 (1 H, ddd, *J* 8.1, 7.3, 1.6, B-1), 7.06 (1 H, dd, *J* 8.1, 1.6, B-2), 7.10 (1 H, dd, *J* 8.4, 2.0, F-6), 7.29 (1 H, m, Bn-4), 7.35 (2 H, m, Bn-3/5), 7.36 (1 H, d, *J* 2.0, F-2) and 7.45 (2 H, m, Bn-2/6); δ_C(24 peaks) 20.62 (OCO*Me*), 55.86 (F3-OMe), 56.26 (B3-OMe), 63.96 ($^3J_{C\gamma,H\alpha}$ 4.3, C-γ), 71.25 ($ArCH_2O$), 113.57 (F-2), 113.80 (B-2), 114.57 (F-5), 117.52 (C-α), 117.96 (B-5), 121.56 (B-6), 122.86 (F-6), 124.49 (B-1), 128.45 (Bn-2/6), 128.55 (Bn-4), 128.69 (F-1), 129.17 (Bn-3/5), 138.48 (Bn-1), 145.26 (B-4), 146.64 (C-β), 148.85 (F-4), 150.39 (F-3), 151.37 (B-3) and 170.45 (O*C*OMe); for (*E*)-**19c-Ac** δ_H 2.08 (3 H, s, OAc), 3.79 (3 H, s, F3-OMe), 3.84 (3 H, s, B3-OMe), 4.87 (2 H, s, CH_2OAc), 5.09 (2 H, s, $ArCH_2O$), 5.81 (1 H, s, α-H), 6.72 (1 H, dd, *J* 8.2, 2.1, F-6), 6.85 (1 H, d, *J* 2.0, F-2), 6.96 (1 H, d, *J* 8.2, F-5), 6.97 (1 H, m, B-6), 7.10 (1 H, dd, *J* 7.8, 1.6, B-5), 7.11 (1 H, dd, *J* 8.1, 1.8, B-2), 7.16 (1 H, ddd, *J* 8.2, 7.1 1.6, B-1), 7.30 (1 H, m, Bn-4), 7.37 (2 H, m, Bn-3/5) and 7.46 (2 H, m, Bn-2/6); δ_C(24 peaks) 20.73 (OCO*Me*), 56.08 (F3-OMe), 56.33 (B3-OMe), 61.70 ($^3J_{C\gamma,H\alpha}$ 7.5, C-γ), 71.42 ($ArCH_2O$), 112.29 (C-α), 113.50 (F-2), 114.41 (B-2), 115.07 (F-5), 121.71 (F-6), 121.89 (B-6), 122.90 (B-5), 126.31 (B-1), 128.44 (Bn-2/6), 128.55 (Bn-4), 129.19 (Bn-3/5), 129.32 (F-1), 138.55 (Bn-1), 144.74 (B-4), 148.37 (F-4), 150.70 (F-3), 152.49 (C-β), 152.64 (B-3) and 170.82 (O*C*OMe).

4-Hydroxy-3-methoxy-β-(2-methoxyphenoxy)styrene **19d**.—1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethanol (guaiacylglycol-β-guaiacyl ether) (93 mg, 0.32 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and was converted into the α-bromide by use of TMSBr[8] (84 mm^3, 0.64 mmol). The quinone methide was generated *in situ* and the elimination was effected by addition of the bromide solution dropwise to a stirred solution of DBU (300 mm^3) in CH_2Cl_2 (5 cm^3). The mixture was stirred for an additional 1 h, and the product was extracted into CH_2Cl_2; the extract was washed with aq. NH_4Cl to remove the base. The products **19d** (84 mg, 97%) were obtained as an oil as a mixture of *Z* and *E* isomers in an approximately 2:1 ratio; for compound (*Z*)-**19d** δ_H 5.56 (1 H, d, *J* 6.8, α-H), 6.65 (1 H, d, *J* 6.8, β-H), 7.53 (1 H, s, ArOH) and 7.65 (1 H, d, *J* 1.9, A-2); for (*E*)-**19d** δ_H 6.16 (1 H, d, *J* 12.4, α-H), 7.21 (1 H, d, *J* 12.4, β-H) and 7.47 (1 H, s, ArOH). Acetylation in CH_2Cl_2 with Ac_2O–DMAP gave the acetates **19d-Ac** in essentially quantitative yield. PLC (multiple development with ethyl acetate–hexane or chloroform) allowed separation of the isomers for full spectral characterization; for (*Z*)-**19d-Ac**, plate crystals, m.p. 103.5–104 °C; δ_H 2.22 (3 H, s, OAc), 3.84 (3 H, s, F3-OMe), 3.88 (3 H, s, B3-OMe), 5.63 (1 H, d, *J* 6.9, α-H), 6.78 (1 H, d, *J* 6.9, β-H), 6.95 (1 H, m, B-6), 6.98 (1 H, d, *J* 8.2, F-5), 7.11 (2 H, m, B-1 and B-2), 7.19 (1 H, m, B-5), 7.20 (1 H, dd, *J* 8.2, 1.9, F-6) and 7.72 (1 H, d, *J* 1.9, F-2); δ_C 20.48 (OCO*Me*), 56.03 (F3-OMe), 56.30 (B3-OMe), 109.26 (C-α), 113.74 (F-2 and B-2), 117.44 (B-5), 121.71 (B-6), 121.91 (F-6), 123.27 (F-5), 125.02 (B-1), 135.08 (F-1), 139.39 (F-4), 143.38 (C-β), 147.25 (B-4), 150.97 (B-3), 151.95 (F-3) and 169.01 (O*C*OMe); for (*E*)-**19d-Ac**, oil, δ_H 2.21 (3 H, s, OAc), 3.81 (3 H, s, F3-OMe), 3.84 (3 H, s, B3-OMe), 6.18 (1 H, d, *J* 12.5, α-H), 6.90–7.15 (7 H, m, ArH) and 7.36 (1 H, d, *J* 12.5, β-H); δ_C 20.26 (OCO*Me*), 56.01 (F3- and B3-OMe), 110.10 (F-2), 111.59 (C-α), 113.70 (B-2), 118.52 (F-6), 119.31 (B-5), 121.51 (B-6), 123.47 (F-5), 125.13 (B-1), 135.17 (F-1), 139.26 (F-4), 143.26 (B-4), 146.50 (C-β), 151.18 (B-3), 152.16 (F-3) and 168.85 (O*C*OMe).

Synthesis of Compounds 4

Compounds **4**, which we expected to be produced as solely the *trans* isomer, were derived in low yield from free-radical coupling of compound **8**.

5-Carboxyvinyl-2-(4-hydroxy-3-methoxyphenyl)-7-methoxy-2,3-dihydrobenzofuran-3-carboxylic Acid Bis(methyl 5-Deoxy-α-L-arabinofuranosid-5-yl) Ester **4a**.—Silver(I) oxide (90 mg, 0.388 mmol) was added to a solution of FA-Ara **8** (107 mg, 0.314 mmol) in acetone (2 cm^3; dried by passage through alumina). After being stirred at ambient temperature in the dark for 72 h (monitoring by TLC), the mixture was filtered through a bed of Celite, evaporated to dryness, and submitted to PLC [CH_2Cl_2–MeOH (20:1)] to yield compound **4a** (59 mg, 55%) as a 50:50 *cis*:*trans* mixture (yellow oil); δ_H 3.289, 3.298, 3.301 and 3.315 (each 3 H, s, 4 × OMe), 3.784 and 3.871 (each 6 H, s, 4 × OMe), 3.85–3.90 (4 × A_f-3), 3.992 and 4.002 (each 2 H, dd, *J* 3.7, 1.7, 4 × A_f-2), 4.072, 4.089, 4.092 and 4.130 (each 1 H, td, *J* 6.7, 3.2, 4 × A_f-4), 4.225 and 4.219 (each 1 H, dd, *J* 11.8, 6.7, 3 × A_f-5_{pro-S}), 4.313 (1 H, dd, *J* 11.8, 6.7, A_f-5_{pro-S}), 4.378, 4.383 and 4.386 (each 1 H, dd, *J* 11.8, 3.2, 3 × A_f-5_{pro-R}), 4.496 (2 H, d, *J* 8.0, 2 × β′-H), 4.524 (1 H, dd, *J* 11.8, 3.2, A_f-5_{pro-R}), 4.770, 4.775, 4.790 and 4.810 (each 1 H, d, *J* 1.7, 4 × A_f-1), 6.011 (1 H, d, *J* 8.0, α′-H), 6.033 (1 H, d, *J* 7.9, α′-H), 6.471 and 6.475 (each 1 H, d, *J* 15.9, 2 × β-H), 6.810 (1 H, d, *J* 8.1, A-5), 6.871 and 6.875 (each 1 H, dd, *J* 8.1, 1.9, 2 × A-6), 7.031 and 7.041 (each 1 H, d, *J* 1.9, 2 × A-2), 7.290 (2 H, t, *J* 1.9, 2 × F-2), 7.383 and 7.402 (each 1 H, br s, 2 × F-6) and 7.667 (2 H, d, *J* 15.9, α-H). A portion of the product mixture was acetylated to give *pentaacetate* **4b** for high-resolution mass spectrometric analysis (Found: M^+, 888.2727. $C_{42}H_{48}O_{21}$ requires *M*, 888.2688).

Synthesis of Compounds 5

Compound **5** (4,8-*exo*-bis-(4-hydroxy-3-methoxyphenyl)-3,7-dioxabicyclo[3.3.0]octan-2-one (monoepoxylignanolide, MEL) was most quickly available as a component of a mixture produced *via* radical coupling of mixed monomers. Silver(I) oxide (560 mg, 2.42 mmol) was added to a solution of coniferyl alcohol **15** (237 mg, 1.32 mmol) and ferulic acid **16** (170 mg, 0.88 mmol) in acetone–water (10:1; 5 cm^3). The mixture was vigorously stirred at ambient temperature for 30 min, and then directly filtered through a bed of Celite. The filtrate was evaporated to give a reddish syrup (387 mg), which was submitted to silica gel chromatography [CH_2Cl_2–MeOH (20:1)]. ^1H NMR analysis of the less polar fraction (37 mg, 9.1%) revealed the presence of pinoresinol **17** (45%), the dilactone **18** (30%), MEL **5a** (20%) and iso-MEL[39] (structure not shown, 5%). This product mixture was acetylated and separated by PLC [chloroform–ethyl acetate (9:1); eluted three times] to afford *diacetate* **5b** (5.5 mg) as an amorphous solid (Found: M^+, 456.1419. $C_{24}H_{24}O_9$ requires *M*, 456.1420); δ_H 2.22 and 2.23 (each 3 H, s, 2 × OAc), 3.45 (1 H, ddddd, $J_{\beta',\beta}$ 9.25, $J_{\beta',\gamma'exo}$ 7.1, $J_{\beta',\gamma'endo}$ 4.8, $J_{\beta',\alpha'}$ 3.6, $J_{\beta',\alpha}$ 0.6, β′-H), 3.72 (1 H, ddd, $J_{\beta,\beta'}$ 9.25, $J_{\beta,\alpha}$ 3.8, $J_{\beta,\gamma'endo}$ 0.5, β-H), 3.82 and 3.83 (each 3 H, s, 2 × OMe), 4.12 (1 H, ddt, $J_{\gamma'endo,\gamma'exo}$ 9.5, $J_{\gamma'endo,\beta'}$ 4.8, $J_{\gamma'endo,\alpha'}$ = $J_{\gamma'endo,\beta}$ = 0.5, γ′-H_{endo}), 4.39 (1 H, ddd, $J_{\gamma'exo,\gamma'endo}$ 9.5, $J_{\gamma'exo,\beta'}$ 7.1, $J_{\gamma'exo,\alpha}$ 0.5, γ′-H_{exo}), 5.29 (1 H, br d, $J_{\alpha',\beta'}$ 3.6, α-H), 5.52 (1 H, dquintet, $J_{\alpha,\beta}$ 3.8, $J_{\alpha,F6} \sim J_{\alpha,F2} \sim J_{\alpha,\beta'} \sim J_{\alpha,\gamma'exo} \sim$ 0.6, α-H), 6.99 (1 H, ddd, $J_{F6,F5}$ 8.1, $J_{F6,F2}$ 1.9, $J_{F6,\alpha}$ 0.7, F-6), 7.01 (1 H, ddd, $J_{A6,A5}$ 8.1, $J_{A6,A2}$ 2.0, $J_{A6,\alpha'}$ 0.6, A-6), 7.04 (1 H, d, $J_{F5,F6}$ 8.1, F-5), 7.08 (1 H, d, $J_{A5,A6}$ 8.1, A-5), 7.14 (1 H, br d, $J_{F2,F6}$ 1.9, F-2) and 7.19 (1 H, br d, $J_{A2,A6}$ 2.0, A-2).

Single-Crystal X-Ray Analysis of Compound 19a

Crystal Data.—$C_{17}H_{18}O_5$, M = 302.3. Orthorhombic, *a* = 8.666(4), *b* = 8.735(4), *c* = 19.664(10) Å, *V* = 1488.5(12) $Å^3$, space group $P2_12_12_1$, *Z* = 4, D_x = 1.349 g cm^{-3}. Prisms. Crystal dimensions 0.1 × 0.4 × 0.4 mm, μ(Cu-Kα) = 0.781 mm^{-1}.

Data Collection and Processing.—Siemens P3f diffractometer, Cu-Kα (λ = 1.541 78 Å) radiation, 113(2) K, highly oriented graphite crystal monochromator, 4.0 ⩽ 2θ ⩽ 114.0°,

Wyckoff scan type, ω scan speed 2.00 to 30.00° min^{-1}, ω scan range 0.50°; stationary crystal and stationary counter background measurements made at beginning and end of scan, each for 20% of the total scan time, standard reflections (−2, 4, 3), (−4, 0, 4) (−2, 2, 8) measured every 150 reflections with a maximum variation of 0.06, index ranges $-9 \leqslant h \leqslant 0$, $0 \leqslant k \leqslant 9$, $-21 \leqslant l \leqslant 21$, 2347 reflections collected, 2016 independent reflections (R_{int} = 8.95%), 1875 observed reflections [$F > 4.0\ \sigma(F)$].

Structure Analysis and Refinement.—Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[44] Distance and angle data were from Allen *et al.*[45] Crystallographic calculations were *via* the Siemens SHELXTL PLUS (VMS) system,[46] using direct methods. Full-matrix least-squares refinement minimizing $\Sigma w(F_o - F_c)^2$, absolute structure η = 1.5(11). Hydrogen atoms were calculated from the Riding model, using isotropic U with the weighting scheme $w^{-1} = \sigma^2(F) + 0.0004\ F^2$. 200 Parameters refined, final R- and R_w-values were 6.23% and 10.34% (6.91% and 10.65% for all data) with a goodness of fit of 3.81. Atomic co-ordinates are given in Table 5, and the X-ray molecular structure is presented as Fig. 1.

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