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REACTIONS OF ß-ARYL LIGNIN MODEL QUINONE METHIDES WITH ANTHRAHYDROQUINONE AND ANTHRANOL[1,2]

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ABSTRACT

Quinone methides prepared in situ from phenylcoumaran and ß-C-1 lignin models which did not contain a ß-hydroxymethyl group, readily formed addition products with anthranol but not with anthrahydroquinone. For ß-aryl lignin models containing the hydroxymethyl group, the retro-aldol reaction (liberating formaldehyde) was so facile under the conditions used that stilbene formation from the quinone methide took precedence over adduct formation.

INTRODUCTION

A great deal of activity has been directed toward the study of the reactions of anthrahydroquinone (AHQ) and anthranol (reduction products of anthraquinone, AQ) with quinone methides of the ß-aryl ether type. It is primarily the reactions of this lignin unit which are responsible for the accelerated cleavage of the lignin macromolecule in alkaline-additive pulping.

Although there is considerable speculation[3] as to whether adducts between AHQ (or anthranol) and ß-ether quinone methides are intermediates in the catalytic cleavage of ß-ether bonds under soda-AQ pulping conditions, there is no doubt that such adducts are readily formed.[4]

ß-Aryl ether quinone methides are not the only quinone methides which can form under pulping conditions; any free-phenolic unit with an α-leaving group (OH, OAr, or OR) can form quinone methides.[5] Indeed, when anthranol, ^{13}C labelled at the 9 and 10 positions, was reacted in base with acetylated milled-wood lignin (conditions which generate lignin quinone methides readily at room temperature), anthranol-lignin adducts were obtained.[6,7] Only two of a multiplicity of peaks in the C-10 region of the ^{13}C NMR spectrum could be attributed to adducts with ß-aryl ether units.[7]

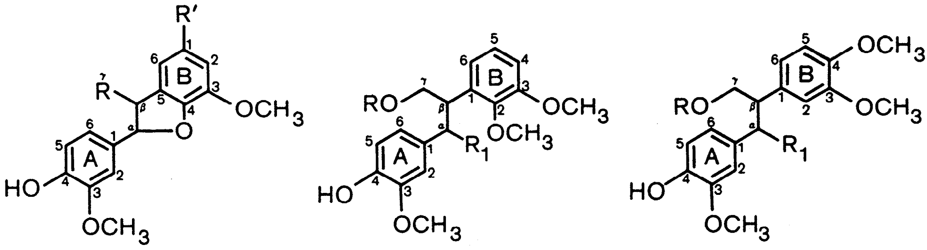
We wished to know if other quinone methides could also trap AHQ or anthranol. If so, it is of interest to determine, firstly, how the presence of AHQ and other species affects the reaction pathways of the ß-aryl units and, secondly, whether reactions involving ß-aryl quinone methides may help account for the considerable loss of "AQ" from the pulping cycle.[8]

The main objective of the work described in this paper was to determine if quinone methides from ß-C linked structures react with AHQ and anthranol and to characterise any adducts formed. Only phenylcoumaran (ß-C-5) and ß-C-1 structures are considered here, although studies on other ß-C linked models are also in progress in our laboratories.

RESULTS AND DISCUSSION

Models

The most readily available phenylcoumaran models are dehydrodiisoeugenol 1,[9] and its reduction product dihydro-

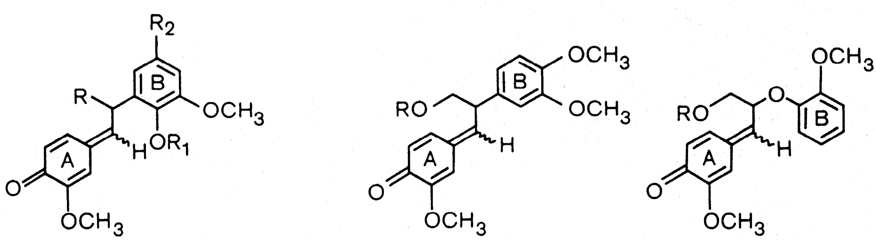


	$\underline{R}$	$\underline{R'}$
$\underline{1}$	CH_3	$CH{=}CH{-}CH_3$
$\underline{2}$	CH_3	$CH_2{-}CH_2{-}CH_3$
$\underline{3}$	CH_2OH	H
$\underline{4}$	CH_2OAc	H
$\underline{5}$	$CH_2OSi^tBuMe_2$	H

	$\underline{R_1}$	$\underline{R}$
$\underline{6}$	OH	H
$\underline{7}$	Br	H
$\underline{8}$	OAc	Ac
$\underline{9}$	OH	Si^tBuMe_2
$\underline{10}$	OAc	Si^tBuMe_2

	$\underline{R_1}$	$\underline{R}$
$\underline{11}$	OH	H
$\underline{12}$	Br	H
$\underline{13}$	OAc	Ac

FIGURE 1 - Models and Derivatives used



	$\underline{R}$	$\underline{R_1}$	$\underline{R_2}$
$\underline{14a}$	CH_3	H	$CH{=}CH{-}CH_3$
$\underline{14b}$	CH_3	H	$CH_2{-}CH_2{-}CH_3$
$\underline{15}$	CH_2OH	H	H
$\underline{16}$	CH_2OAc	H	H
$\underline{17}$	$CH_2OSi^tBuMe_2$	H	H
$\underline{18}$	CH_2OH	CH_3	H
$\underline{19}$	CH_2OAc	CH_3	H
$\underline{20}$	$CH_2OSi^tBuMe_2$	CH_3	H

	$\underline{R}$
$\underline{21}$	H
$\underline{22}$	Ac

	$\underline{R}$
$\underline{23}$	H
$\underline{24}$	Ac

FIGURE 2 - Quinone methides

dehydrodiisoeugenol 2 (Figure 1). Use of 2 rather than 1 removes the complication of further reactions of the vinyl side chain which are not characteristic of the phenylcoumaran moiety of lignin.

Although the use of these easily synthesised models is valuable in developing methods for the study of adduct formation, it is preferable to use a more representative model such as 3 (Figure 1) which possesses the hydroxymethyl group present in most lignin side chains. The presence of this group markedly influences the course of important reactions.

A model representing a 'ring-opened' ß-C-5 unit (which could not cyclise to a phenylcoumaran) was also required in our studies. The erythro isomer of model 6 (Figure 1), in which the B-ring phenolic group is methylated, was prepared using essentially the method of Brunow and Lundquist.[10]

A base-stable t-butyldimethylsilyl protecting group in compounds 5, 9, and 10, increased the stability of the quinone methides with respect to polymerisation and removed the possibility of retro-aldol reactions.

Model 11 was synthesised to represent free phenolic ß-C-1 units in lignin in which the B-ring phenol is etherified.

Anthranol and AHQ Adducts with Quinone Methides of ß-aryl Models

Alpha-aryl ethers such as compounds 1-5 (Figure 1) are known[5] to (reversibly) generate quinone methides at a significant rate even at 10°C in 1M NaOH (Scheme 1). Therefore, attempts to form adducts from quinone methides 14-17 (Figure 2) were made by addition of models 1 to 5 directly to solutions of anthranol or AHQ in base. These reactions gave products as summarised in Table 1.

The anthranol adduct 27a from dehydrodiisoeugenol 1 polymerised slowly on standing to give the polystyryl derivative

TABLE 1

Approximate yield (%) data for adduct reactions.[a]

Model		Anthranol			AHQ		
		Adduct[b]	Starting material	Stilbene	Adduct	Starting material	Stilbene
1	27a	70(97:3)	30	0	0	100	0
2	27b	70	30	0	0	100	0
3		0	0	100	0	0	100
4	31	50(90:10)	50	0	–	–	–
5	33	50(80:20)	50	0	–	–	–
8	30	90(75:25)[c]	0	0	0	•	•
10	34	95(50:50)[d]	0	0	–	–	–
13	36	35(95:5)[e]	•	0	–	–	–

a Conditions: 2 eq anthranol or AHQ; 1M NaOH (except 0.3 M for 4 to minimize hydrolysis of the γ-OAc group); 50°C; 1 hr (15 min for 8).

b Ratio of erythro:threo isomers (in brackets) determined from H-1 NMR after acetylation.

c 75% yield after flash chromatography.

d 80% after flash chromatography. Isolated erythro 41% and threo 39% as pure fractions.

e Single reaction only; yield not optimised; other products not characterised. NMR of crude material indicated possibility of threo isomer, approximately 90:10 erythro:threo.

• Product not observed.

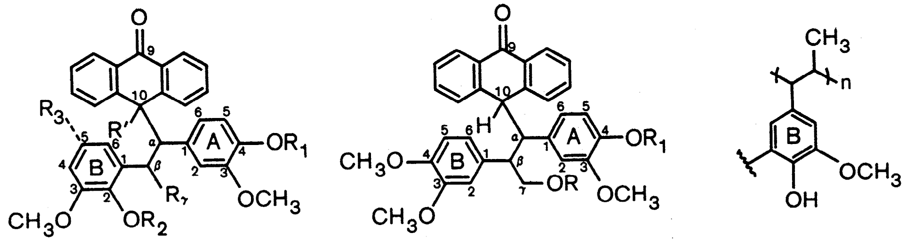
37. Polymerisation could be prevented by addition of trace quantities of butylated hydroxytoluene.

Generation of the quinone methide 18 from the ring-opened phenylcoumaran model 6 at moderate temperatures required the α-OH to be replaced with a better leaving group. Attempts to form 7, the α-bromide, from 6 using bromotrimethylsilane[11] were unsuccessful due to spontaneous loss of formaldehyde, and formation of 4-hydroxy-3,2',3'-trimethoxystilbene from the bromide. However, quinone methide 19 could be generated *in situ* from the free phenolic diacetylated model 8 in base. As there was no possibility of quinone methide 19 reverting to a phenylcoumaran by an internal cyclisation, the yield (Table 1) of anthranol adduct was substantially higher from model 8 than from the true phenylcoumarans 1-5.

Analogously, the ß-C-1 quinone methide 22, generated from the free phenolic diacetylated model 13, was used for adduct reactions.

Silylated model 9 could be brominated using bromotrimethylsilane[11] in chloroform. Treatment of this solution with aqueous potassium carbonate gave relatively stable solutions of quinone methide 20. Alternatively, quinone methide 20 was generated from the free-phenolic α-acetate 10 in base. Reaction of anthranol with quinone methide 20 gave adduct 34 (after acetylation) in very high yield as a 50:50 mixture of *erythro* and *threo* isomers. Unlike the parent acetylated adducts 32, these were readily separated by tlc.

A further point is apparent from Table 1. Whereas anthranol adducts form readily from these quinone methides, attempts to form the corresponding AHQ adducts (e.g., R'=OH of 27a, Figure 3) using both aqueous and organic solvents, at temperatures ranging from 0°C to 80°C, were unsuccessful, presumably for a combination of steric and electronic reasons. It has been noted previously[4,12] that AHQ adds less readily



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	R′	R	R_1	R_2	R_3
27a	H	CH_3	H	H	$CH{=}CH{-}CH_3$
27b	H	CH_3	H	H	$CH_2{-}CH_2{-}CH_3$
28a	H	CH_3	Ac	Ac	$CH{=}CH{-}CH_3$
28b	H	CH_3	Ac	Ac	$CH_2{-}CH_2{-}CH_3$
29	H	CH_2OAc	H	H	H
30	H	CH_2OAc	H	CH_3	H
31	H	CH_2OAc	Ac	Ac	H
32	H	CH_2OAc	Ac	CH_3	H
33	H	$CH_2OSi^tBuMe_2$	Ac	Ac	H
34	H	$CH_2OSi^tBuMe_2$	Ac	CH_3	H

	R	R_1
35	H	H
36	Ac	Ac

FIGURE 3 - Adduct structures

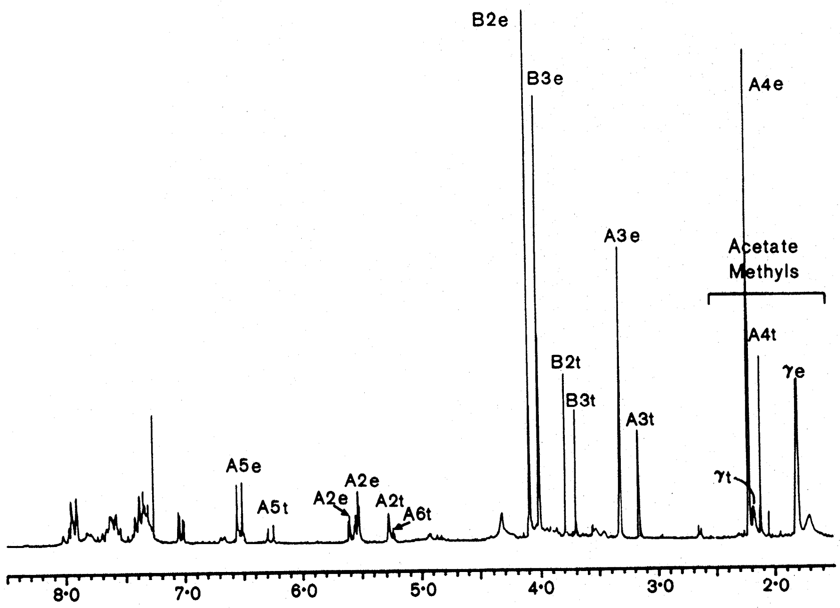


FIGURE 4 - Partial 200 MHz H-1 NMR spectrum of β-C-5 adducts 32
t = threo, e = erythro

than anthranol to ß-aryl ether quinone methides and it has also been shown[4,12] that, in competition studies, anthranol adducts are formed in overwhelming preference.

Stereochemistry and NMR Spectra of Adducts

Despite the high kinetic stereoselectivity observed[4,13] for threo adducts from ß-ether quinone methides (e.g., 23-24), both adduct isomers can be detected from attack of anthranol on most of the ß-aryl quinone methides (Figure 4 and Table 1).

The ß-aryl adducts 27-36 (Figure 3), like the ß-aryl ether adducts,[4,14,15] have fascinating NMR characteristics due to their conformations in solution. For example, in the erythro isomer of 32 (which is analogous to the threo isomer in ß-ether adducts because of the convention of group assignments) the A-ring is clearly situated over the anthracenyl ring system, as is evidenced by the highly shielded ring A methoxyl and the ring A protons (Figure 4). However, the minor threo isomer is quite unlike the erythro isomer[14] of ß-ether adducts in that ring A protons are more intensely shielded. The threo γ-acetate methyl chemical shift is also anomalous, appearing at δ 2.0 compared with a normal shift of δ1.8. This methyl group is presumably in a deshielding region of the anthracenyl ring system and/or the other aromatic rings. In addition, the B-ring methoxyl protons experience substantial shielding, indicating their positions within the shielding regions of the anthracenyl ring system and/or ring A. Conformations of erythro- and threo-32, postulated from the information in their spectra, are shown in Figure 5.

Similar features appear in the spectra of ß-C-1 adducts (e.g., Figure 6) indicating that small changes in the substitution on ring B do not significantly alter the adduct conformations. Selected NMR data for these adducts are given in

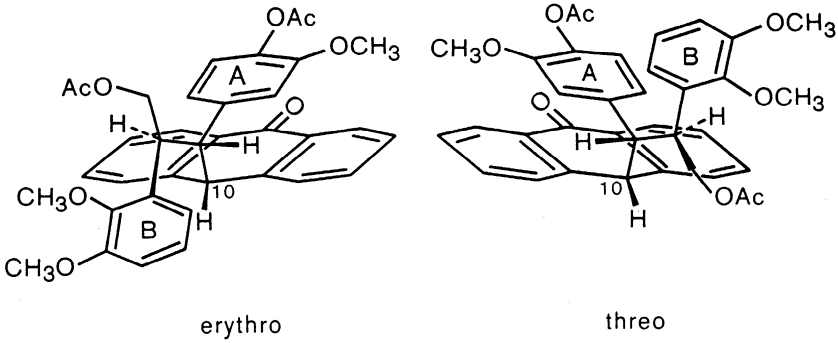


FIGURE 5 - Postulated conformations of erythro and threo isomers of compound 32

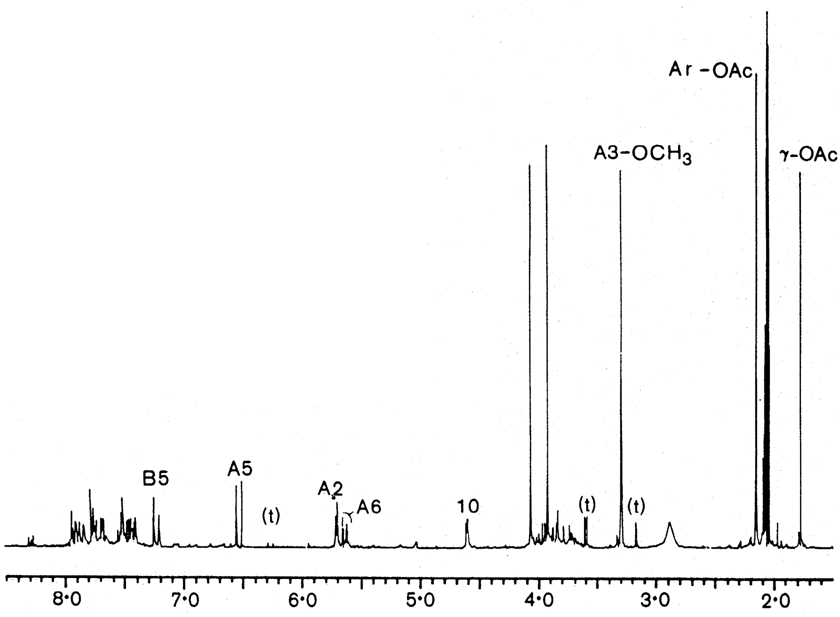


FIGURE 6 - Partial 200 MHz H-1 NMR spectrum of crude ß-C-1 adducts 36 in acetone-d_6, (t) indicates peaks from the threo isomer

TABLE 2

Selected ¹H NMR data for adducts

Adduct	Isomer(1)	Solv.(2)	MHz	Methoxyls			Acetate methyls			Aromatic protons			α	β	γ's	10	tBu	MeSiMe
				A3	B3	B4/B2(3)	A4	B2		A2	A5	A6						
<u>27a</u>	e	C	60	3.37	4.00	–	–	–	–	5.40	6.42	5.50	(3.6-3.85)		0.93	4.47		
<u>27b</u>	e	A	200	3.35	4.00	–	–	–	–	5.37	6.40	5.51	.	.	0.93	4.47		
<u>28b</u>	e	A	200	3.29	3.93		2.22	2.47	–	5.48	6.53	5.48*	(3.47-3.87)		0.89	4.48		
<u>31</u>	e	C		3.35	3.98	–	2.24	2.50	1.88	5.60*	6.55	5.60*	.	.	.	.		
	t	C		3.19	3.64	–	2.10	2.30	1.92	?	?	?	.	.	.	.		
<u>32</u>	e	C		3.28	3.94	4.10	2.15	–	1.70	5.50	6.50	5.55	.	.	.	.		
	t	C		3.08	3.60	3.72	2.10	–	2.02	5.28	6.22	5.20	.	.	.	.		
<u>34</u>	e	C		3.28	3.95	4.05	2.20	–	–	5.50	6.55	5.60	.	.	.	.	0.70	-0.30, -0.40
	t	C		3.15	3.55	3.65	2.00	–	–	5.35	6.21	5.20	.	.	.	.	1.00	0.04, 0.06
<u>36</u>	e	C	90	3.29	3.98, 4.08		2.20		1.78	5.49	6.53	5.53	*	3.51	*	4.50		
	e	A	200	3.29	3.92, 4.06		2.14	–	1.77	5.69	6.51	5.62	**	3.63	**	4.59		
	t(4)	A	200	3.16	3.58, 3.59		.	.	.	.	6.24	.	.	.	.	.		

(1) e = <u>erythro</u>, t = <u>threo</u>

(2) C = $CDCl_3$, A = acetone-d_6

(3) B4 in adducts derived from β-C-1 models <u>11</u>-<u>13</u>; B2 from models <u>6</u>-<u>10</u>

(4) From a 95:5 e:t mixture (Fig. 5)

* Hindered rotation exchanging these positions, m, 3.59-3.85

** Hindered rotation exchanging these positions, m, 3.79-3.85

. Indicates resonances which are not resolvable due to coincident chemical shifts and/or to line broadening caused by hindered rotation.

TABLE 3

Selected ^{13}C NMR data for adducts

Adduct	Isomer[(1)]	Solv.[(2)]	MHz	Methoxyls	Acetate methyls	Cα	Cβ	Cγ	C10	C9	Acetate C=O	SiMe	Si^{t}Bu
<u>27a</u>													
<u>27b</u>	e	C	22.5	55.6, 56.0	-	62.0	33.9	21.6	45.9	183.6	-	-	-
<u>28b</u>	e	C	22.5	55.5, 56.0	20.6	62.0	34.2	22.6	45.6	183.1	168.7	-	-
<u>31</u>	e	C	22.5	55.4, 56.2	20.6, 20.6, 20.6	58.4	38.4	67.7	45.1	182.9	167.8, 168.6, 171.0	-	-
	e	A	50	56.4, 56.4	20.4, 20.6, 20.6	58.6	39.3	68.1	45.6	183.0	168.4, 168.4, 168.5		
	t[(3)]	A	50	.	20.5, 20.8, .	58.1	.	67.7	45.9	182.9	168.5, 168.5, 168.5	-	-
<u>32</u>	e	C	50	55.7, 55.5, 61.2 (B2)	20.5, 20.6	59.1	37.9	67.5	45.1	183.1	168.6, 170.4	-	-
	t[(4)]	C	50	55.2, 55.6, 60.4 (B2)	20.4, 21.0	57.9	37.9	67.5	45.2	182.7	168.4, 171.1	-	-
	e	A	50	55.6, 55.9, 61.5 (B2)	20.4, 20.6	59.4	39.0	68.1	45.6	183.1	168.5, 170.5	-	-
	t	A	50	55.3, 56.1 60.7 (B2)	20.3, 21.0	58.4	37.5	68.0	45.5	182.9	168.3, 171.2	-	-
<u>34</u>	e	C	50	55.5, 55.6, 61.4 (B2)	20.5	58.4	40.7	65.9	45.1	183.3	168.6	-5.9, -6.0	25.8
	e	A	50	55.6, 55.9, 61.5 (B2)	20.4	58.7	41.9	66.7	45.6	183.2	168.5	-5.6, -5.7	26.2
	t[(5)]	C	50	55.3, 55.5, 60.5/.6 (B2)	20.5	56.8/57.7	39.2	65.8/67.3	44.7/44.9	182.9/183.1	168.5	-3.6, -5.8	25.9
	t	A		55.3, 55.7, 60.7 (B2)	20.3	58.8	40.0	66.6	45.2	183.1	168.4	-3.2, -5.7	26.2
<u>36</u>	e	C	22.5	55.3, 55.9, 56.2	20.5, 20.5	58.5	46.0	68.0	44.6	182.7	168.5, 170.3		
		A	50	55.6, 56.2, 56.6	20.4, 20.6	58.8	47.0	68.6	45.2	183.0	168.6, 170.6		

(1) e = <u>erythro</u>, t = <u>threo</u>

(2) C = $CDCl_3$, A = acetone-d_6

(3) From a 90:10 e:t mixture

(4) From a 75:25 e:t mixture

(5) Two rotamers frozen out on NMR time scale

Tables 2 and 3. Full spectral details and assignments may be given in a separate publication.

The ^{13}C NMR C-10 chemical shifts of these adducts in acetone-d_6 allow a more complete analysis of the C-10 region of the ^{13}C NMR of the anthranol-lignin adduct reported previously.[7] Figure 7 is a highly expanded plot of the C-10 region of the anthranol-lignin adduct on which is shown the positions of ß-aryl ether, phenylcoumaran, and ß-C-1 adducts. There is little doubt that adducts between these three unit types account for most of the resonances in this region.

Several of the adducts exhibited hindered rotation phenomena[4,15] in their proton and ^{13}C NMR spectra. The effect of temperature on the spectra of these adducts was far more complex than that observed for certain ß-aryl ether adducts,[15] and indicated that the behaviour was not simply due to rotation about a single bond. One compound, threo-**34**, was fully resolved at ambient probe temperature into two rotamers (60:40 ratio) on the ^{13}C NMR time-scale (Figure 8). The broader resonances from the major rotamer indicate that either the T_2 relaxation times are shorter or that further fluxional behaviour is occurring in the major rotamer that is not significant in the minor rotamer.

The observed stereoselectivity of anthranol attack can reasonably be attributed to the quinone methide conformations. Figure 9 shows the two major conformers expected[16] for ß-aryl quinone methides. If the conformation does not significantly alter the charge density at the alpha carbon and R is sterically less demanding than Ar (as expected for R = Me, CH_2OH, CH_2OAc), **A** would be the major conformer. Attack from the less hindered side would lead to the erythro adduct. As R becomes larger (e.g., $CH_2OSi{}^tBuMe_2$), rotamer **B** becomes significant, resulting in more threo product.

For reasons that are not clear, these ß-aryl quinone methides are markedly less stable toward polymerisation than ß-aryl ether quinone methides and, at modest concentrations, are observed only transiently at room temperature. Attempts to characterise them by NMR techniques[16] are in progress.

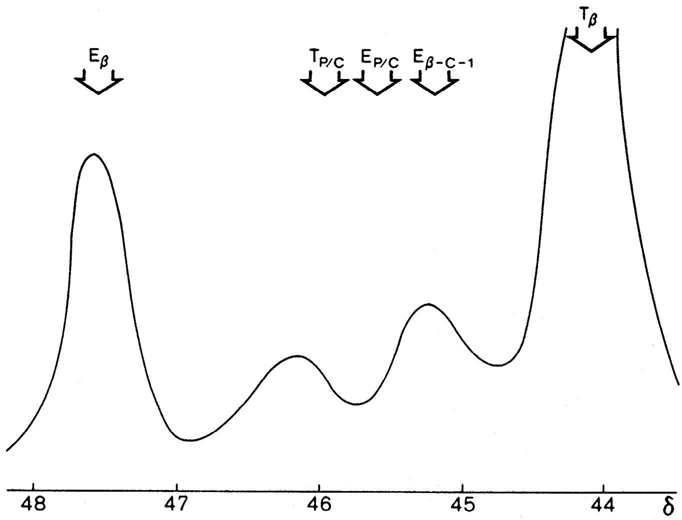


FIGURE 7 - ^{13}C NMR (in acetone-d_6) of the C-10 region of an anthranol-lignin adduct[7] and chemical shifts of model adducts (E = <u>erythro</u>, T = <u>threo</u>, β = β-aryl ether, P/C = phenylcoumaran)

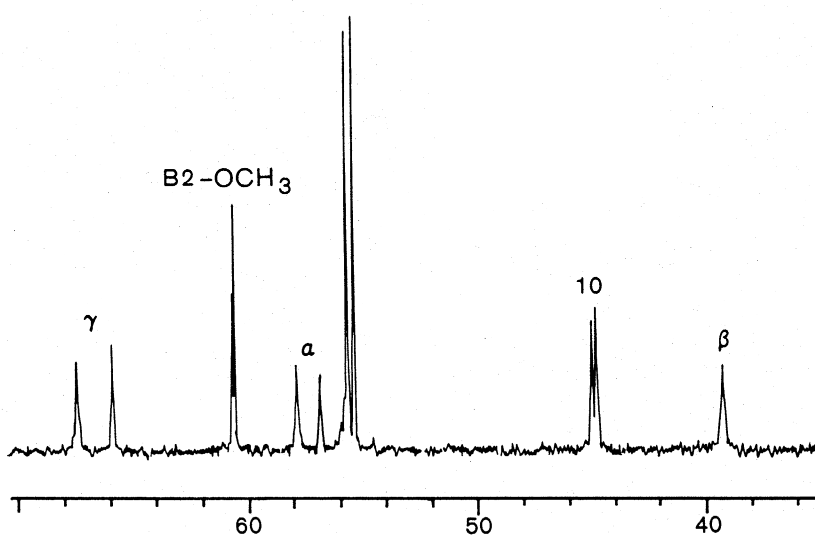
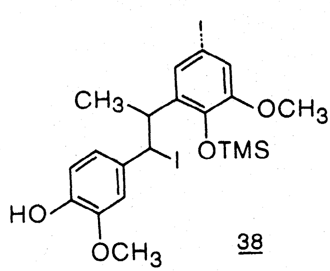


FIGURE 8 - Partial ^{13}C NMR of adduct <u>threo</u>-<u>34</u> showing hindered rotation

The Phenylcoumaran Quinone Methide: Competition Between Anthranol Adduct Formation and the Reversal Reaction to the Phenylcoumaran

Formation of quinone methides from phenylcoumarans 1-5 in base is clearly reversible (Scheme 1). The assumed steady state quinone methide concentration is too low to be detectable by conventional UV-visible or NMR spectroscopy. The reverse reaction to the phenylcoumaran must therefore be very rapid. Nevertheless, nucleophiles such as anthranol, obviously compete for the quinone methide.

In order to ascertain how effectively anthranol can compete with the quinone methide reversal reaction, the α-iodide 38 was prepared from dihydrodehydrodiisoeugenol, 2, by treatment with iodotrimethylsilane in chloroform. It was assumed that, on treatment with base, the phenolic TMS group would rapidly hydrolyse and that the quinone methide 14b would rapidly form by elimination of iodide. The phenylcoumaran 2 was isolated in high yield from such a reaction. Addition of the iodide 38 to a solution of anthranol in base and workup within 5 minutes gave a ratio of adduct 27b to phenylcoumaran 2 of approximately 10:90. Since only traces of adduct 27b were detected when phenylcoumaran 2 is reacted with anthranol under the same conditions for 5 minutes, it is concluded that anthranol attack is about 10% as rapid as the recyclisation reaction.



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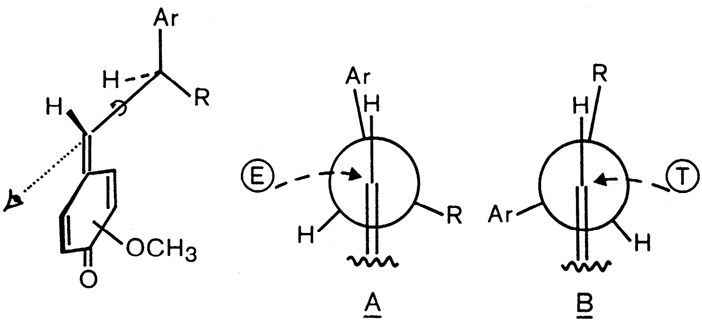


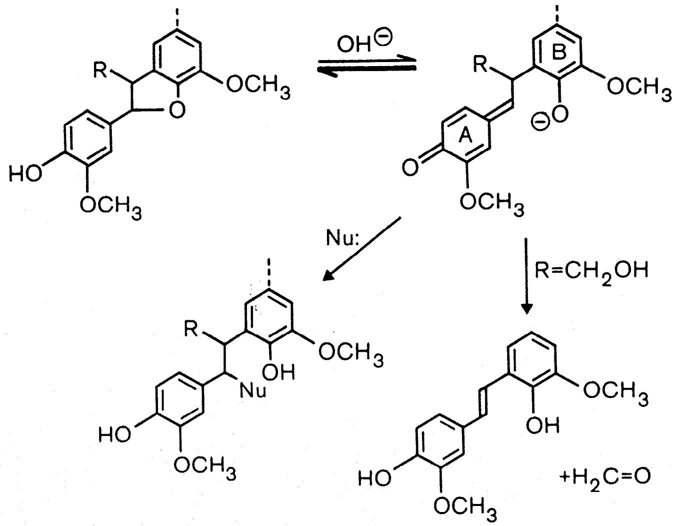
FIGURE 9 - Major conformers of ß-aryl quinone methides

The Phenylcoumaran Quinone Methide: Competition Between Adduct Formation and the Retro-Aldol Reaction

During much of this work, quinone methides were most conveniently generated from free-phenolic acetates or t-butyldimethylsilylated compounds, but the use of these derivatives precludes one very important reaction - the retro-aldol elimination of formaldehyde. To relate the results of model studies to reactions involving lignin itself, it is essential that the model contains the hydroxymethyl group.

Despite its surprising effectiveness at trapping quinone methides,[12] not even anthranol could compete against the retro-aldol elimination of formaldehyde from quinone methides 15, 18 or 21 to give stilbenes. The reaction therefore follows the same course as in the absence of the additive (Schemes 1 and 2).[17]

This point illustrates the pitfalls of using inappropriately substituted or derivatised models. Acetylated models,[4,18] or acetylated lignin itself,[6,7] are frequently used to allow in-situ generation of quinone methides at room temperature. But the protection afforded to the hydroxymethyl group by acetylation means that formaldehyde loss by a retro-aldol reaction cannot compete in subsequent quinone methide reactions. This is not so



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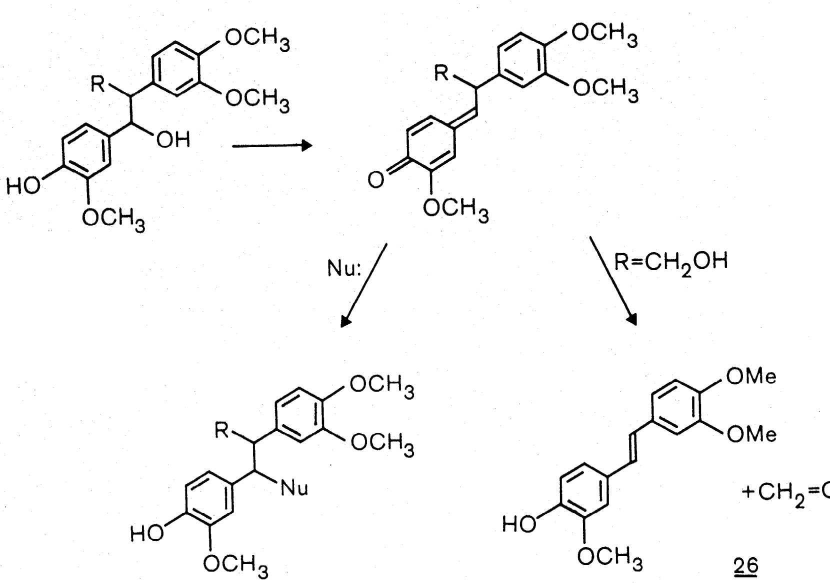
SCHEME 1 - Reactions of phenylcoumarans



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SCHEME 2 - Reactions of ß-C-1 models

critical in the case of ß-aryl ether quinone methides since anthranol and AHQ can add to quinone methide 23 efficiently before the retro-aldol reaction (to give the styryl ether) can occur.[12] However, in phenylcoumaran and ß-C-1 models, the retro-aldol reaction entirely dominated the reaction of representative quinone methides 15, 18, or 21 (with the ß-CH_2OH substituent) whereas adducts readily formed from the acetylated quinone methides 16, 19, or 22, or the silylated derivatives 17 or 20. Thus, reactions on acetylated milled-wood lignin with anthranol, where adducts other than ß-ether adducts appear to be observed in the C-13 NMR spectra,[6,7] may not be representative of reactions of the underivatised quinone methides.

CONCLUSIONS

Adduct formation between ß-aryl quinone methides and anthranol, but not AHQ, occurs readily, but only when the possibility of formaldehyde elimination from the quinone methide is removed. Consequently, the reactivity of lignin phenylcoumaran and ß-C-1 units in soda-AQ pulping is not expected to be altered by the presence of AQ species. Conversely, it is not expected that AQ losses can be attributed to reactions of its reduction products with ß-aryl quinone methides.

EXPERIMENTAL

^{1}H NMR spectra were determined in $CDCl_3$ or acetone-d_6 on a CW Varian T-60, a JEOL FX90Q, or a Bruker AC200 FT spectrometer using tetramethylsilane as an internal reference. ^{13}C NMR spectra were determined in $CDCl_3$ or acetone-d_6 on a JEOL FX90Q (22.5 MHz) or Bruker AC200 (50 MHz) FT spectrometer using tetramethylsilane as an internal reference. ^{29}Si NMR spectra were determined in $CDCl_3$ on a Bruker AC200 (39.8 MHz) spectrometer using a broadband proton-decoupled ^{29}Si DEPT[19,20] pulse sequence with 1/2J delays of 72 ms, and a θ pulse of approximately 17° (optimised). ^{29}Si-^{1}H coupling constants (^{2}J = 6.53, ^{3}J = 6.96 Hz) were determined from the ^{29}Si satellites in ^{1}H NMR spectra. Mass spectra were determined on an HP 5985 quadrupole GC/MS under electron impact conditions using 70 eV ionizing energy (direct insert probe).

General Methods

Preparation of TBDMS derivatives[21]

The primary alcohol (1.0 eq), t-butyldimethylsilylchloride (1.5 eq), and diazabicyclo[5,4,0]undec-7-ene (DBU, 1.4 eq) in CH_2Cl_2 (10 ml/mmole 1,2-diarylpropane-1,3-diol) were stirred for 40 minutes at 40°C. The products were extracted into CH_2Cl_2 and washed three times with saturated aqueous NH_4Cl. The organic phase was dried over $MgSO_4$ and the solvent removed to give the silyl ethers in ca. 95% yield after purification.

Quinone Methides

Quinone methides 14-24 were generated in situ either from the free phenolic phenylcoumarans (1-5), or from the free phenolic α-acetylated derivatives (8, 10, 13).

Anthrahydroquinone (AHQ and AHQ^{2-})

Solutions of AHQ^{2-} in aqueous 1 M or 0.3 M NaOH containing, or free from, sodium dithionite were prepared as described in reference 4.

Anthranol

Solutions of the anion of anthranol were prepared by refluxing a mixture of anthrone in 1 M or 0.3 M NaOH (20-50 ml) under nitrogen until dissolution was complete (about 1 hour). The solutions were then cooled to the required temperature.

AHQ or Anthranol Adducts

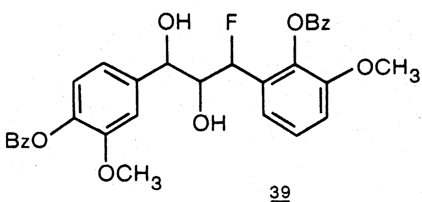
To a solution of AHQ or anthranol (2 eq) in base (at the temperature given in Table 1) was added the quinone methide precursor in solid form or as a solution in a small volume of CH_2Cl_2. After the appropriate time (usually 1 hour for phenylcoumarans and 15 minutes for γ-acetate quinone methide precursors), the mixture was neutralised with 5% H_2SO_4 and extracted with $CHCl_3$ (2 X). The chloroform extract was dried over $MgSO_4$ and the solvent removed.

Specific Syntheses

Dehydrodiisoeugenol (1). Dehydrodiisoeugenol was prepared in 50% yield from isoeugenol.[9]

Dihydrodehydrodiisoeugenol (2). Dehydrodiisoeugenol (1, 1.0 g, 3.07 mmole) in 95% ethanol was hydrogenated at atmospheric pressure over 5% Pd/C (2.5 mg) for 2 hours (yield quantitative). Crystallisation from petroleum ether (100-120°C fraction) gave white needles m.p. 89-91°C.

Compound 3 was prepared in 30% overall yield using the method of Brunow and Lundquist.[10] The major by-product of the $BF_3.Et_2O$ rearrangement of the chalcone epoxide was identified as fluorohydrin 39 (yield 42%).



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Compound 39 was a white crystalline solid: m.p. 120-122°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.09 (1H, dd, $J_{OH-\beta}$ = 5.4 Hz, J_{OH-F} = 0.9 Hz, β-OH), 2.24 (1H, dd, $J_{OH-\alpha}$ = 4.9 Hz, J_{OH-F} = 1.5 Hz, α-OH), 3.81 (3H, s, OCH_3), 3.89 (3H, s, OCH_3), 4.06 (1H, dddd, $J_{\beta F}$ = 25.6 Hz, $J_{\beta\alpha}$ = 6.8 Hz, $J_{\beta-OH}$ = 5.4 Hz, $J_{\beta\gamma}$ = 2.4 Hz, Hβ), 4.74 (1H, dd, $J_{\alpha\beta}$ = 6.8 Hz, $J_{\alpha-OH}$ = 4.9 Hz, Hα), 4.97 (1H, d, J = 10.9 Hz, B ring benzyl CH), 5.04 (1H, d, J = 10.9 Hz, B ring benzyl CH), 5.12 (2H, s, A ring benzyl CH_2), 5.98 (1H, dd, $J_{\gamma F}$ = 45.9 Hz, $J_{\gamma\beta}$ = 2.4 Hz, Hγ), 6.70-7.20 (6H, m, Ar-H), 7.30-7.50 (10H, m, benzyl Ar-H). Mass Spectrum m/z: 518 (M^{+}, 0.1), 256 (5), 242 (3), 238 (3), 227 (3), 165 (3), 137 (4), 92 (8), 91 (100), 65 (10). ^{13}C NMR of diacetate (22.49 MHz, $CDCl_3$) δ: 20.1 (α-$OCOCH_3$), 20.8 (β-$OCOCH_3$), 55.7, 55.8 (3,3' OCH_3), 70.8 (4-benzyloxy CH_2), 72.5 (d, $^{3}J_{\alpha F}$ = 7 Hz, α), 73.6 (d, $^{2}J_{\beta F}$ = 18 Hz, β), 74.3 (2'-benzyloxy CH_2), 86.7 (d, $^{1}J_{\gamma F}$ = 178 Hz, γ), 111.3 (2), 112.8 (4'), 113.4 (5), 118.8 (d, $^{3}J_{6'F}$ = 9 Hz, 6'), 120.3 (6), 123.1 (5'), 127.2 (benzyl 3,5), 127.7 (benzyl 4), 128.4 (benzyl 2,6), 129.5 (1), 129.6 (d, $^{2}J_{1'F}$ = 20 Hz, 1'), 136.9 (benzyl 1), 137.8 (benzyl 1'), 144.0 (d, $^{3}J_{2'F}$ = 9 Hz, 2'), 148.1 (3), 149.2 (4), 152.0 (3'), 168.7 (α-$OCOCH_3$), 169.7 (β-$OCOCH_3$).

Compound 4. Acetylation of compound 3 to give the diacetate, followed by removal of the phenolic acetate[22] with pyrrolidine (1.2 eq) in $CHCl_3$ for 30 minutes, gave 4 as a clear oil in 90% overall yield. ^{1}H NMR (200 MHz, $CDCl_3$ δ: 2.00 (3H, s, γ-$OCOCH_3$) 3.30 (1H, m, Hβ), 3.78 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 4.36 (1H, dd, $J_{\beta\gamma 1}$ = 7.6 Hz, $J_{\gamma 1\gamma 2}$ = 11.1 Hz, γ_1), 4.47 (1H, dd, $J_{\beta\gamma 2}$ = 5.5 Hz, $J_{\gamma 1\gamma 2}$ = 11.1 Hz, γ_2), 5.72 (1H, d, $J_{\alpha\beta}$ = 6.9 Hz, Hα), 5.80 (1H, s, Ar-OH), 6.8-7.2 (6H, m, Ar-H).

Compound 5. t-Butyldimethylsilylation prior to debenzylation in the synthesis of compound 3 gave 5 (88% overall yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.04, 0.06 3H, (2 x 3H, 2s, $SiMe_2$), 0.89 (9H, s, $SiBu^t$), 3.65 (1H, m, Hβ), 3.84 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 3.80-4.00 (2H, m, Hγ's), 5.55 (1H, d, $J_{\alpha\beta}$ = 5.8 Hz, Hα), 5.60 (1H, s, Ar-OH), 6.80-7.00 (6H, m, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: -5.31, -5.28 ($SiMe_2$), 18.3 (Me_3CSi), 25.9 (Me_3CSi), 54.2 (β), 56.0 (OMe's), 65.5 (γ), 87.9 (α), 108.7 (A2), 112.1 (B4), 114.3 (A5), 117.1 (B6), 119.1 (A6), 121.2 (B5), 128.0 (A1), 133.7 (B1), 144.5 (B2), 145.7 (A4), 146.7 (A3), 148.3 (B3).

Compound 6 was prepared by modifying the procedure for synthesis of compound 3.[10] Condensation of 2,3-dimethoxybenzaldehyde 40 with the benzyl ether of acetovanillone following the method of reference 10 gave the chalcone 1-(4-benzyloxy-3-methoxyphenyl)-3-(2,3-dimethoxyphenyl)-2-propen-1-one 41 as a yellow oil. Crystallisation from hot ethanol gave 41 as yellow crystals m.p. 94-95°C (yield 76%). ^{1}H NMR (60 MHz, $CDCl_3$) δ: 3.80 (6H, s, OCH_3), 3.90 (3H, s, OCH_3), 5.18 (2H, s, CH_2Ph), 6.70-7.80 (11H, m, Ar-H), 7.40 (1H, d J = 16 Hz, Hβ), 8.08 (1H, d, J = 16 Hz, Hγ). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ: 55.8, 55.9 (3,3'-OCH_3), 61.6 (2'-OCH_3), 70.7 (benzyl CH_2), 111.3 (C2), 112.2, (C4'), 114.0 (C5), 119.6 (C6'), 122.8, (C6) 123.2 (C5'), 124.1 (Cβ), 127.2 (benzyl C3, C5), 128.0 (benzyl C4), 128.6 (benzyl C2, C6), 129.2 (C1), 131.6 (C1'), 136.2 (benzyl C1), 138.7 (Cγ), 148.8 (C2'), 149.6 (C3), 152.3 (C3'), 153.1 (C4), 188.7 (α-C=O). Mass spectrum m/z: 404 (M^{+}, 12), 373(13), 254(19), 91(100).

Epoxidation was more simply carried out by stirring chalcone 41 (0.05 mole) in pyridine (160 ml) with aqueous NaOCl (5.4%, 160 ml) for 3 hours.[23] Workup gave a white solid which was recrystallised from hot ethanol to give the chalcone epoxide 1-(4-benzyloxy 3-methoxyphenyl)-3-(2,3-dimethoxyphenyl)-2,3-epoxypropan-1-one 42 as white needles m.p. 123-124°C (76% yield). ^{1}H NMR (60 MHz, $CDCl_3$) δ: 3.79 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 4.20 (1H, d, J = 2 Hz, Hβ), 4.32 (1H, d, J = 2 Hz, Hγ), 5.21 (2H, s, CH_2Ph), 6.70-7.70 (11H, m, Ar-H). ^{13}<u>C NMR</u> (22.5 MHz, $CDCl_3$) δ: 54.9 (Cβ), 55.3, 55.4 (3-, 3'-OCH_3), 59.5 (Cγ), 60.5 (2'-OCH_3), 70.2 (benzyl CH_2), 110.1 (C2), 111.8 (C4'), 112.3 (C5), 116.5 (C6'), 122.7 (C6), 124.0 (C5'), 126.8 (benzyl C3, C5), 127.6 (benzyl C4), 128.1 (benzyl C2, C6), 128.4, 129.1 (C1, C1'), 135.6 (benzyl C1), 147.6 (C2'), 149.6 (C3), 152.0 (C3'), 152.7 (C4), 191.0 (C=O).

Rearrangement of <u>42</u> with $BF_3.Et_2O$ in Et_2O followed by reduction of the crude mixture with $NaBH_4/OH^-$ gave a colorless oil which crystallised on standing. Recrystallisation from CH_2Cl_2/pet. ether (40-60°C) gave 1-(4-benzyloxy-3-methoxyphenyl)-2-(2,3-dimethoxyphenyl)-propan-1,3-diol <u>43</u>, m.p. 122.5-123.5°C (yield 61%, c.f. 38% in synthesis of <u>3</u>[10]). No fluorohydrin was detected among the by-products. ^{1}<u>H NMR</u> (60 MHz, $CDCl_3$) δ: 2.50 (2H, br s, OH), 3.55 (3H, s, OCH_3), 3.60 (3H, s, OCH_3), 3.78 (3H, s, OCH_3), 3.20-4.20 (3H, m, Hβ, Hγ's), 4.90 (1H, d, J = 6 Hz, Hα), 5.05 (2H, s, CH_2Ph), 6.60-7.60 (11H, m, Ar-H). ^{13}<u>C NMR</u> (22.49 MHz, $CDCl_3$) δ: 47.8 (Cβ), 55.6, 55.7 (3-OCH_3, 3'-OCH_3), 60.5 (2'-OCH_3), 63.8 (Cγ), 71.0 (benzyl CH_2), 74.8 (Cα), 110.5 (C2), 111.0 (C4'), 113.7 (C5), 118.8 (C6), 121.1 (C6'), 123.7 (C5'), 127.3 (benzyl C3, C5), 127.6 (benzyl C4), 128.4 (benzyl C2, C6), 132.7 (C1), 135.9 (C1'), 137.1 (benzyl C1), 147.3 (C2'), 147.7 (C3), 149.3 (C4), 152.6 (C3').

Debenzylation of <u>43</u> in wet dioxane with a catalytic amount of 5% Pd/C under 1 atm H_2 for 2 hours gave <u>6</u> as a colorless oil, yield 100%. ^{1}<u>H NMR</u> (60 MHz, $CDCl_3$) δ: 2.60 (2H, br s, OH), 3.62 (3H, s, OCH_3), 3.66 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 3.30-4.40 (3H, m, Hβ, Hγ's), 4.90 (1H, d, J = 6 Hz, Hα), 6.60-7.00 (6H, m, Ar-H). ^{13}<u>C NMR</u> (50 MHz, $CDCl_3$) δ: 48.2 (Cβ), 55.6, 57.7 (3,3'-OCH_3), 60.7 (2'-OCH_3), 63.9

(Cγ), 75.1 (Cα), 109.4 (C2), 111.1 (C4'), 114.1 (C5), 119.5 (C6), 121.0 (C6'), 124.0 (C5'), 132.8 (C1), 134.3 (C1'), 145.2 (C4), 146.5 (C3), 147.8 (C2'), 152.8 (C3').

Compound 7. Attempted bromination of 6 using bromotrimethylsilane[11] gave only 4-hydroxy-3,2',3'-trimethoxystilbene, presumably via HBr and formaldehyde elimination from bromide 7. ^{1}H NMR (60 MHz, $CDCl_3$) δ: 3.80 (9H, s, OCH_3), 6.40-7.20 (8H, m, ArH and vinyl H).

Compound 8. Acetylation prior to debenzylation in the above synthesis of compound 6 gave 8 in 74% overall yield for the two steps. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.80 (3H, s, γ-$OCOCH_3$), 1.86 (3H, s, α-$OCOCH_3$), 3.68 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 4.05 (2H, m $H\gamma_1$, ß), 4.25 (1H, dd, $J_{\beta\gamma 2}$ = 5.8 Hz, $J_{\gamma 1 \gamma 2}$ = 9.8 Hz, $H\gamma_2$), 5.60 (1H, s, Ar-OH), 6.05 (1H, d, $J_{\alpha\beta}$ = 5.8 Hz, Hß), 6.70-7.05 (6H, m, Ar-H). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ: 20.7 (γ-$OCOCH_3$), 21.0 (α-$OCOCH_3$), 42.1 (ß), 55.6, 55.8 (A3, B3 OCH_3), 60.6 (B2-OCH_3), 64.7 (γ), 75.5 (α), 110.0 (B4), 111.2 (A2), 114.2 (A5), 120.3, 120.3 (A6, B6), 123.6 (B5), 130.6(A1), 131.9 (B1), 145.6, 146.3, 147.8 (A3, A4, B2), 152.5 (B3), 169.8 (α-$OCOCH_3$), 170.7 (γ-$OCOCH_3$).

Compound 9. t-Butyldimethylsilylation prior to debenzylation in the above synthesis of compound 6 gave 9 in 92% overall yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ: -0.049, -0.043 (2 x 3H, 2s, $SiMe_2$), 0.88 (9H, s, Bu^tSi), 3.65 (3H, s, OCH_3), 3.65 (1H, m, Hß), 3.68-3.78 (2H, m, Hγs), 3.76 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 5.14 (1H, d, J = 4.5 Hz, Hα), 5.55 (1H, s, ArOH), 6.60-7.00 (6H, m, Ar-H).

Compound 10. t-Butyldimethylsilylation, followed by acetylation prior to debenzylation in the above synthesis of compound 6 gave 10 in 85% overall yield over the three steps. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.15, 0.18 (2 x 3H, 2s, $SiMe_2$), 1.05 (9H, s, Bu^tSi), 1.98 (3H, s, α-$OCOCH_3$), 3.82 (3H, s,

OCH_3), 3.86 (1H, m, Hβ), 3.94 (3H, s, OCH_3), 3.90-4.10 (2H, m, Hγ's), 3.98 (3H, s, OCH_3), 6.00 (1H, s, Ar-OH), 6.34 (1H, d, $J_{\alpha\beta}$ = 7.8 Hz, Hα), 6.80-7.40 (6H, m, Ar-H).

Compound 11. Compound 11 was prepared by amalgamating synthetic schemes from Berndtsson *et al.*[24] and Nakatsubo and Higuchi.[25] Thus, benzyl vanillin was condensed with homoveratric acid to give an acid 44 corresponding to compound 6 in ref. 24 in 90% yield as a mixture of *threo* and *erythro* isomers in a 3:1 ratio. The two isomers were separated by fractional crystallisation from acetone-hexane. *Erythro*-44 was a white crystalline solid; m.p. 175-182°C. ^{1}H NMR (90 MHz, $CDCl_3$) δ: 3.67, 3.68, 3.73 (9H, 3s, methoxyls), 3.83 (1H, d, $J_{\beta\alpha}$ = 9 Hz, Hβ), 5.05 (2H, s, CH_2Ph), 5.32 (1H, d, $J_{\alpha\beta}$ = 9 Hz, Hα), 6.63-7.31 (11H, m, aromatics), 9.60 (1H, bs, COOH). *Threo*-44 was a white crystalline solid, m.p. 150-152°C; ^{1}H NMR (90 MHz, $CDCl_3$) δ: 3.67, 3.68, 3.73 (9H, 3s, methoxyls), 3.83 (unresolved, Hβ), 5.00 (2H, s, CH_2Ph), 5.14 (1H, d, $J_{\alpha\beta}$ = 9 Hz, Hα), 6.63-7.31 (11H, m, aromatics), 9.60 (1H, bs, COOH).

As the diborane reduction of acids 44 did not proceed well, each isomer of the acid 44 was methylated with diazomethane to give the ester 45 corresponding to compound 5 of ref. 25 in quantitative yield (approximately 70% yield after 1 recrystallisation). *Erythro*-45 was a white crystalline solid; m.p. 145.5-147°C; ^{1}H NMR (60 MHz, $CDCl_3$) δ: 3.55 (3H, s, acetate methyl) 3.80 (1H, d, $J_{\beta\alpha}$ = 7, Hβ), 3.83, 3.86, 3.86 (9H, 3s, methoxyls) 5.12 (2H, s, CH_2Ph), 5.18 (1H, d, $J_{\alpha\beta}$ = 7, Hα), 6.65-7.37 (11H, m, aromatics): ^{13}C NMR (22.5 MHz, $CDCl_3$) δ: 51.9 (ester methyl), 55.9 (methoxyls), 59.2 (Cβ), 71.0 (CH_2Ph), 74.9 (Cα), 172.9 (ester carbonyl); mass spectrum m/z 434 ($M^{+\cdot}$ - H_2O, 0.5), 242 (13), 210 (32), 151 (41), 91 (100). *Threo*-45 was a light yellow crystalline solid (ex acetane-hexane); m.p. 131.5-132.5°C; ^{1}H NMR (60 MHz, $CDCl_3$) δ: 3.72 (3H, s, acetate methyl), 3.75 (unresolved, Hβ), 3.70, 3.70, 3.77 (9H, 3s, methoxyls), 5.03 (2H, s, CH_2Ph), 5.18 (1H, d, $J_{\alpha\beta}$ = 8 Hz, Hα), 6.57-7.33 (11H, m, aromatics); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ: 52.2 (ester methyl), 55.8 (methoxyls), 59.5 (Cβ), 71.0 ($\underline{C}H_2Ph$), 76.4 (Cα), 174.0 (ester carbonyl); mass spectrum, m/z 434 (M^{+} - H_2O, 0.5), 242 (11), 210 (44), 151 (43), 91 (100).

Debenzylation, acetylation and reduction, essentially as described in ref. 25, gave the required β-C-1 model 11. The triacetate of threo-11 was a colourless oil; ^{1}H NMR (60 MHz, $CDCl_3$) δ: 2.05, 2.14, 2.31 (9H, 3s, acetate methyls), 3.35 (1H, m, Hβ); 3.73, 3.80, 3.88 (9H, 3s, methoxyls), 4.49 (2H, m, Hγs), 6.10 (1H, d, J = 9, Hα), 6.58-6.95 (6H, m, aromatics); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ: 20.5, 20.8, 21.1 (acetate methyls), 49.5 (Cβ), 55.7 (methoxyls), 64.3 (Cγ), 75.9 (Cα), 168.6 ($PhO\underline{C}OCH_3$), 169.7 (α-$O\underline{C}OCH_3$), 170.8 (γ-$O\underline{C}OCH_3$; mass spectrum m/z 460 (M^{+}, 9), 400 (6), 358 (5), 237 (14), 223 (100), 195 (50), 181 (37), 164 (96), 153 (64), 43 (56).

The free phenol diacetate 13 was prepared by acetylation of the ester 45 followed by LAH reductions, re-acetylation and catalytic removal of the benzyl group. Threo-13 was a colourless oil; ^{1}H NMR (60 MHz, $CDCl_3$) δ: 2.03, 2.10 (6H, 2s, acetate methyls), 3.49 (1H, m, Hβ), 3.70, 3.75, 3.83 (9H, 3s, methoxyls), 4.43 (2H, m, Hγ's), 5.98 (1H, d, $J_{\alpha\beta}$ = 8.4, Hα), 6.53-6.75 (6H, m, aromatics).

Anthranol Adducts

Conditions, yields and erythro:threo ratios are given in Table 1; selected NMR data are given in Table 2 and ^{13}C NMR data in Table 3.

Adduct 27a: Prepared from model 1. The erythro isomer was isolated by flash chromatography using chloroform as eluant. Acetylation gave adduct 28a. On standing, compound 27a spontaneously polymerised, presumably to the styrene polymer 37 as indicated by the line broadening, the loss of the allylic methyl resonance, and the appearance of a new (broad) aliphatic methyl resonance (δ ca. 1).

Adduct 27b: Prepared from model 2. The erythro isomer was isolated by prep. tlc using EtOAc:hexane as eluant. Acetylation gave adduct 28b.

Adduct 29: Prepared from model 4. Acetylation gave 31. Attempts to separate threo and erythro isomers were unsuccessful.

Adduct 30: Prepared from model 8. Acetylation gave 32. Small scale separation on analytical tlc plates using multiple elution with EtOAc-hexane gave 300 μg pure erythro adduct.

Adduct 33: Prepared from model 5, followed by acetylation.

Adduct 34: Prepared from model 10, followed by acetylation. The ^{29}Si NMR spectra also showed hindered rotation features. Threo-34: δ 19.96, 19.99; erythro-34 δ 19.39 (broad).

Competition for the Quinone Methide Between Anthranol Adduct Formation and Reversal to the Phenylcoumaran

Model 2 (160 mg, 1.0 eq) in $CDCl_3$ was treated with trimethylsilyl iodide (117 mg, 1.2 eq) for 3 minutes to give the α-iodide 38 (as evidenced by ^{1}H NMR, δ 5.5, $J_{\alpha\beta}$ ca. 10 Hz). This solution was rapidly added to a solution of anthranol (190 mg) in aqueous base (1 M NaOH), stirred for 5 minutes, then neutralised and extracted with $CHCl_3$, etc., as in the general method for adduct formation. The resultant product mixture was approximately 10% anthranol adduct 27b to 90% phenylcoumaran 2 by ^{1}H NMR.

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