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NOVEL HYDROXY LIGNANS FROM THE HEARTWOOD OF *GMELINA ARBOREA*

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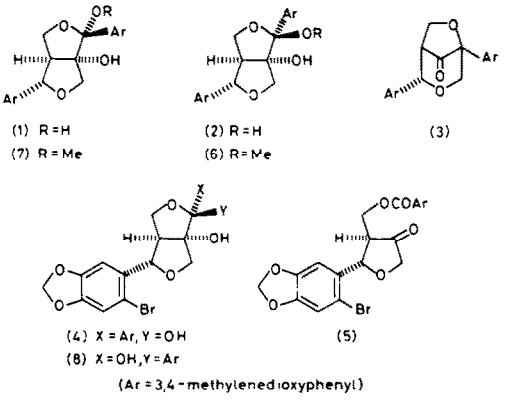
Abstract—The structures of six new lignans isolated from the heartwood of *Gmelina arborea* have been determined. They are 6″ - bromo - isoarboreol, 4 - hydroxysesamin, 4,8 - dihydroxysesamin, 1,4 - dihydroxysesamin (gummadiol), 2 - piperonyl - 3 - hydroxymethyl - 4 - (α - hydroxy - 3,4 - methylenedioxybenzyl) - 4 - hydroxytetrahydrofuran, and the 4 - O - glucoside of 4 - epigummadiol. The ^1H and ^{13}C NMR and mass spectra of these compounds and their derivatives are discussed, and the structure previously assigned to a germination inhibitor from *Aegilops ovata* is questioned.

We have previously reported the isolation of a number of new lignans including arboreol (**1**), isoarboreol (**2**), and gmelanone (**3**) from the heartwood of *Gmelina arborea*.[1] From this same sample of *Gmelina arborea* (obtained from Berhumpur) we have also isolated 6″ - bromo - isoarboreol (**4**),[2] $C_{20}H_{17}BrO_8$, m.p. 190°, $[\alpha]_D$ −22.5°, a rare example of a halogen containing product derived from a higher plant.



The ^1H and ^{13}C NMR spectra of **4** (Tables 1 and 2) were very similar to those of **1** and **2** and established that the aliphatic portion of the molecule was unchanged. The Br atom must therefore be attached to one of the aromatic rings, and comparison of the ^{13}C NMR spectrum of 6″ - bromo - isoarboreol (**4**) with that of isoarboreol (**2**) showed that one of the signals due to C-6′ or C-6″ had been replaced by a new quaternary signal at 111.60 ppm (Table 2).

The mass spectral fragmentation of **4** (Fig. 1) is also very similar to that of **1** and **2**, involving sequential loss of H_2O and CH_2O from the molecular ion to give *m/e* 416/8, and then loss of HBr to yield an ion of *m/e* 336. The presence of an ion at *m/e* 239/241, losing Br to give *m/e* 160, and the absence of *m/e* 161 ($ArCH{=}\overset{+}{C}HCH_2$) suggested that the Br atom was attached to the C-6 aryl group. This was confirmed by periodate oxidation which gave the keto-ester (**5**), m.p. 122°, $\nu_{C=O}$ 1760 cm^{-1}, which could be hydrolysed to piperonylic acid and a keto-alcohol containing bromine. The ^1H and ^{13}C NMR spectra

Table 1. ^1H NMR spectra of 6″ - bromo - isoarboreol (**4**), isoarboreol (**2**) and the keto-ester (**5**).*

Proton	6″-Bromo-isoarboreol (4) (d_6-acetone)	Isoarboreol (2) ($CDCl_3$)	Keto-ester (5)[ø] ($CDCl_3$)
4a	5.89 dd (9, 4)	6.14 dd (8, 2)	5.49 d (4.5)
4e	5.5 dd (9, 9)	5,60 dd (8, 7)	
5	7.29 m	7.31 m	7.28 m
6	4.98 d (5)	5.47 d (6)	4.51 d (10)
8a	6.56 d (10)	6.66 d (10)	6.00 d (17)
8e	6.36 d (10)	6.28 d (10)	5.64 d (17)
OCH_2O	3.99, 4.05	4.08, 4.12	4,06, 4.09
arom.	2.8 - 3.4 m	2.8 - 3.4 m	2.5 - 3.4 m
OH	4.00, 4.33	6.63, 6.96	-

*Values are given in τ, coupling constants (in Hz) in brackets. All assignments are supported by appropriate spin decoupling experiments and correct integration.

[ø]The numbering used is that of the arboreols for convenience of comparison.

Table 2. ^{13}C NMR spectra*

Carbon	Isoarboreol (2)	6''-Bromo isoarboreol (4)	Keto-[a] ester (5)	Paulownin (18)	Gummadiol (10)	Gummadiol acetate (14)	γ-Lactone from gummadiol (15)	Triol[a] (12)	Acetate[a] of triol (20)	Sesamin (19)	4-Hydroxy sesamin (9)	Acetate of 4-hydroxy sesamin (21)	γ-Lactone of 4-hydroxy sesamin (22)	4,8-Dihydroxy sesamin (11)	Diacetate of 4,8-dihydroxy sesamin (24)	Dilactone from 4,8-dihydroxy sesamin (25)
1	94.99	94.09	211.40	91.74	91.99	94.63	86.20	84.16	90.03	54.24	53.16	52.61	53.22	60.37	58.51	48.16
5	60.26	59.60	54.59	60.58	66.60	64.70	58.79	61.39	53.40		62.14	61.12	49.90			
2	102.66	101.53	165.23	87.48	88.00	88.79	85.58	73.23	75.19	85.61	88.14	89.00	83.25	85.32	85.92	81.93
6	90.07	87.73	81.09	85.88	83.39	83.67	82.63	83.97	83.39		83.30	83.28	84.26			
4	68.56	68.98	60.36	71.58	101.04	100.20	174.90	60.45	60.97	71.55	101.71	101.12	176.37	101.17	100.31	174.86
8	76.80	76.33	71.88	74.98	75.10	75.81	77.20	75.69	73.94		72.26	72.51	72.58			
1'1"	135.02	133.84	131.47	129.39	129.75	129.94	128.94	134.49	120.44	134.93	135.42	135.12	132.85	136.54	134.68	131.67
		134.78	123.3	134.79	135.09	133.89	134.64	136.22	133.66		136.09	135.47	134.17			
		147.09	147.51		147.23	147.08	146.80	146.91	147.30		147.25	147.26	147.08			
3'3"	147.88	147.39	147.98	147.33	147.71	147.34	146.94	146.96	147.57	146.86	147.32	147.32	147.84	147.16	147.62	148.28
4'4"	148.33	147.48	148.41	148.21	147.75	147.49	147.18	147.27	147.76	147.74	148.08	148.08	148.19	147.91	148.22	148.45
		147.63	151.6		148.04	147.95	147.37	147.65								
	106.77	106.84	107.30	106.91	106.23	106.35	106.62	107.24	106.64		106.29	106.11	105.59			
2'2"	107.17	107.54	107.79	107.49	107.49	107.61	107.62	107.41	107.82	106.32	107.07	106.60	105.83	107.30	106.35	105.58
5'5"	108.23	107.83	109.27	108.23	108.14	108.14	107.93	107.61	107.90	107.96	108.08	108.06	108.19	107.89	108.22	108.59
	108.30	112.00	112.60	108.56	108.36	109.28	108.01	108.40	108.33		108.25	108.35	108.39			
6'6"	119.62	119.46	125.30	119.79	119.21	119.52	119.76	119.99	119.97	119.13	119.23	119.18	118.60	118.97	119.81	118.98
	120.09	111.60	113.61	120.14	120.09	123.41	121.24	120.86	122.39		120.04	119.80	118.86			
OCH_2O	101.27	100.94	101.72	101.12	101.04	101.05	101.01	100.81	100.96	100.89	101.11	101.12	101.05	101.02	101.24	101.52
	101.47	101.63	101.96	101.24	101.16				101.17				101.31			
						169.05			170.48							
						169.66			169.39							
OAc						21.18			169.22			170.01			169.75	
						20.73			20.66			21.26			21.22	
									20.98							
									22.18							

*Measurements are given as ppm downfield from TMS. All assignments are supported by off-resonance decoupling expts.
[a]Carbon atoms numbered as in the arboreol series for ease of comparison.

of the keto-ester (Tables 1 and 2) are in complete accord with the proposed structure, as is its mass spectrum (Experimental). In the ^{13}C spectrum the ketone carbon comes at 211.40 ppm while the ester carbon comes at 165.2 ppm.

We then examined a sample of *Gmelina arborea* from Vijayawada which proved to have a markedly different lignan composition from the Berhumpur sample. It did not contain **1**, **2**, **3** or **4**, but instead produced five new lignans as well as β-sitosterol and 3,4 - methylenedioxy-

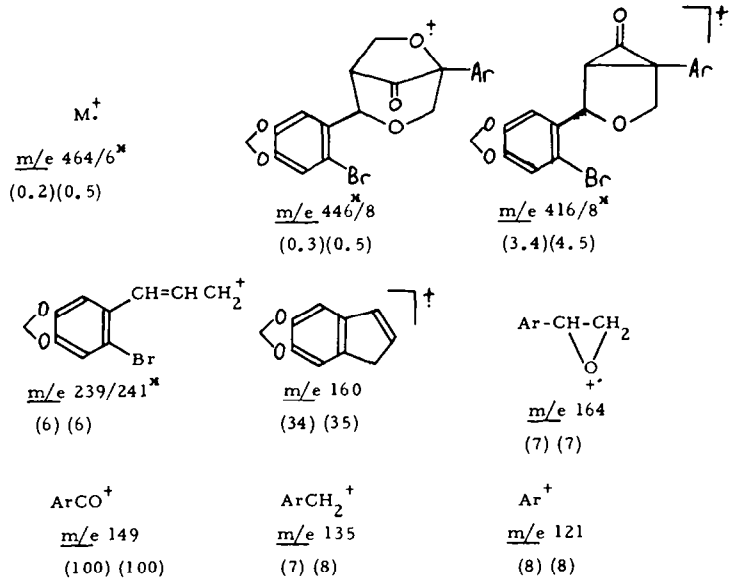


Fig. 1. Fragments in the mass spectra of 6″-bromo-isoarboreol (**4**) and 6″-bromo-arboreol (**8**).*

*These peaks were accurately mass measured (Experimental).

[a]In this and in all following formula Ar = 3,4 - methylenedioxyphenyl. Figures in first brackets are relative intensities for **4**, in the second brackets for **8**.

6″ - Bromo - isoarboreol (**4**) could be prepared by treating methyl isoarboreol (**6**) with bromine in chloroform. Similarly when methyl arboreol (**7**) was treated with bromine in chloroform 6″ - bromo - arboreol (**8**), m.p. 162°, $[\alpha]_D$ −6°, was obtained. The NMR, IR, and mass spectra of 6″ - bromo - isoarboreol and its isomer were almost superimposable and both gave the keto-ester (**5**) upon periodate oxidation. However periodate oxidation of 6″ - bromo - isoarboreol required 10 hr whereas periodate oxidation of 6″ - bromo - arboreol required only 4.5 hr, indicating that the naturally occurring compound is a derivative of isoarboreol rather than arboreol. The demethylation which accompanies bromination in these conditions clearly proceeds with retention of configuration at C-2, presumably due to direct attack by the bromide anion on the Me group.

ycinnamaldehyde,[3] previously isolated by Hänsel from Sassafras root.[4]

The major component is a new dihydroxy lignan, gummadiol (**10**),[5] $C_{20}H_{18}O_8$, m.p. 130°, $[\alpha]_D$ +32°, which readily afforded a diacetate (**14**), $C_{24}H_{22}O_{10}$, m.p. 140°, $[\alpha]_D$ +31°, but unlike arboreol (**1**) and isoarboreol (**2**), did not undergo periodate cleavage. The NMR and mass spectra (Tables 3 and 4) of **10** confirm that the molecule contains the 3,7 - dioxabicyclo[3.3.0]octane skeleton,[6,7] and has two 3,4 - methylenedioxyphenyl groups. In the mass spectrum the ions at *m/e* 338 and 161, which are characteristic of the arboreols, are of low intensity (1 and 3%), while the peak at *m/e* 176 (88%) suggests that there is an oxygen atom at C-4 (see Fig. 2 and Table 3). Also of some significance (see later) is the peak at *m/e* 159 (2%), which is more intense in the spectrum of the acetate (9%), and

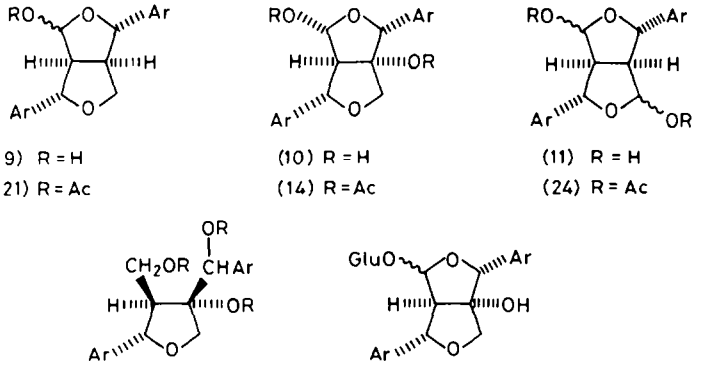


Table 3. Mass spectra of 4-hydroxysesamin (9), gummadiol (10), and the diacetate (25) of 4,8-dihydroxysesamin

m/e	Relative abundance (%) of significant peaks		
	(9)	(10)	(25)
470	-	-	35 $(M^+)^*$
386	-	5 $(M^+)^*$	-
370	22 $(M^+)^*$	3 *	-
369	4	1	-
368	15*	2*	-
352	6	-	-
351	-	-	5
350	-	1*	10
323	8	-	-
322	9	-	-
247	-	-	9
219	-	2	22*
210	-	7*	-
203	7	1	-
202	19*	1	7
201	-	1	37
194	12	1	-
193	-	1	14
192	-	5*	18
191	8	1	-
190	9	1	19
189	14	1	13
178	8	3	-
177	8	14	56
176	19	88*	51*
175	-	26	-
174	9	1	-
173	21	1	15
172	6	-	-
166	-	4	-
164	10	3	-
163	-	2	-
162	6	2	-
161	41	3	-
159	6	2	51*
152	11	10	11
151	58	100*	100
150	34	39	19
149	100	100*	87
148	9	15	-
147	5	31	-
146	-	11	-
135	50	11	60
131	44	3	11
122	19	15	-
121	19	24	8

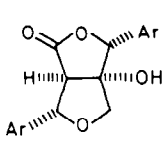
*These peaks have been accurately mass measured (see Experimental).

appears to be characteristic of lignans with a hydroxyl group at the 4-position. It presumably arises by breakdown of the ion ar *m/e* 350.

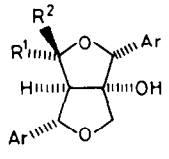
The ^{1}H NMR spectrum of **10** (Table 4) showed two benzylic signals, one appearing as a singlet at 4.86τ confirming that there is an OH group at C-1 as in gmelinol and paulownin,[8,9] and the other as a doublet at 5.15τ (J = 6 Hz). The chemical shifts of the H-8 protons (6.08 and 5.96τ), both of which are seen as doublets (J = 10 Hz), indicate that the aryl group at C-2 is equatorial.[6] The methine proton at high field due to H-5 was coupled to H-6 (5.15τ) and also to one proton (4.6τ) at C-4. This latter signal was moved downfield by 0.86 ppm in the diacetate (**14**), and so there can be no doubt as to the attachment of a hydroxyl group at C-4 in gummadiol.

The ^{13}C NMR spectrum (Table 2) of gummadiol was in full accord with structure **10**. The signal due to C-1 comes at 91.99 ppm corresponding to those of gmelinol, paulownin and arboreol, but C-4 is at 101.04 ppm as compared with 71.58 ppm in paulownin. Furthermore oxidation with chromium trioxide in pyridine gave the γ-lactone (**15**), $C_{20}H_{16}O_8$, m.p. 157°, $\nu_{C=O}$ 1770 cm^{-1} with C-4 at 174.90 ppm as expected.[10]

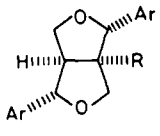
Treatment of **10** at room temperature with methanol containing a few drops of conc hydrochloric acid gave an O-Me derivative (**16**), m.p. 176°, $[\alpha]_D$ −22.5°, thus confirming that **10** is a hemi-acetal. The same reaction at reflux gave a different monomethyl ether (**17**), m.p. 182°, $[\alpha]_D$ +36°, this presumably being the thermodynamically



(15)



(16) R^1 = H, R^2 = OMe
(17) R^1 = OMe, R^2 = H



(18) R = OH
(19) R = H

Table 4. ^{1}H NMR spectra of gummadiol and its derivatives

Proton	Gummadiol (10) ($CDCl_3$)	Diacetate (14) ($CDCl_3$)	Axial methyl ether (16) ($CDCl_3$)	Equatorial methyl ether (17) ($CDCl_3$)	γ-Lactone (15) ($CDCl_3$)	Triol[a] (12) ($CDCl_3$-d_6DMSO)	Triacetate (20)[a] of triol ($CDCl_3$)
2	4.86s	4.63	5.05s	5.08s	4.60s	5.23 br.d.(3)[b]	3.99s
4	4.6 br.[c]	3.74d (2)	5.02d (2)	4.99d (2)	-	6.27m (2H)[c]	5.68m (2H)
5	7.15dd (2,6)	6.65d (2,6)	7.07d (2,6)	7.26dd (2,6)	6.77d (4)	7.7m	6.79m
6	5.15d (6)	5.02d (6)	5.16d (6)	5.16d (6)	4.80d (4)	5.52d (6)	5.28d (6)
8a	6.08d (10)	5.72d (10)	6.05s (2H)	6.14s (2H)	6.07d (10)	6.72d (10)	6.13d (10)
8e	5.96d (10)	5.48d (10)			5.87d (10)	6.46d (10)	5.89d (10)
OCH_2O	4.12s, 4.14s	4.09s,4.10s	4.09s	4.05s,4.07s	4.06s,4.10s	4.10s,4.12s	4.07s,4.10s
OH	8.38 br.s	-	5.43	4.99	7.31s	4.6d (4) 4.9 br.t. 5.73 br.s	-
$OCOCH_3$	-	7.94s,8.30s	-	-	-	-	7.93s 7.94s 8.03s
OCH_3	-	-	6.57s	6.64s	-	-	-
arom.	3.0 - 3.4m	3.0 - 3.4m	3.0 - 3.3m	3.0 - 3.4m	3.0 - 3.4m	2.95 - 3.30m	3.1 - 3.4m

[a]Carbon atoms numbered as in gummadiol for ease of comparison.
[b]Becomes singlet after shaking with D_2O.
[c]Signal sharpens after shaking with D_2O.

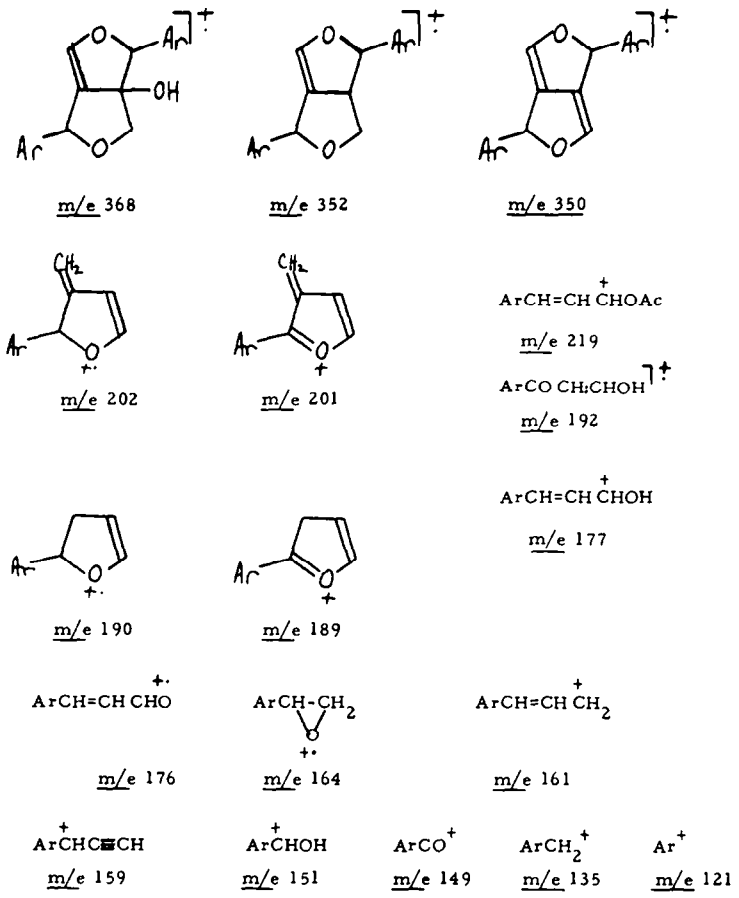
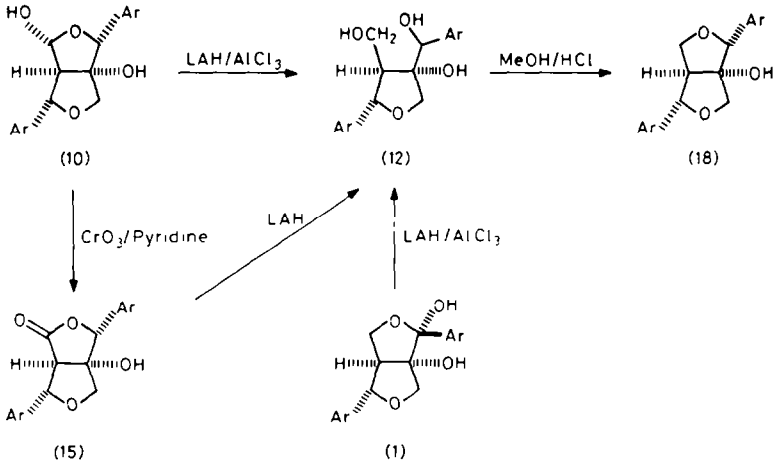


Fig. 2. Fragments in the mass spectra of 4-hydroxysesamin (**9**), gummadiol (**10**), and 4,8-dihydroxysesamin diacetate (**25**).

more stable product with the alkoxyl group equatorial. Comparison of the specific rotations of the two monomethyl ethers with that of gummadiol itself (+32°) suggests that the 4-OH group in gummadiol is equatorial.

This leaves only the stereochemistry at C-6 of gummadiol to be established, and this was achieved (Scheme 1) by its conversion into the triol (**12**), either by LAH reduction of the γ-lactone (**15**) or by direct reduction of gummadiol with LAH–$AlCl_3$. The same triol (**12**) could also be prepared from arboreol (**1**) by reduction with LAH–$AlCl_3$. When the triol **12** was refluxed with methanolic hydrogen chloride it underwent cyclization to give (+)-paulownin (**18**). These transformations confirm the identity of the configuration at C-1, C-5 and C-6 in **1**, **12**, **18** and **10** and of course establish that in gummadiol there is an equatorial aryl group at C-6. In connecting gummadiol, paulownin and arboreol with the triol **12**, the structure of which is unequivocally proven by the proton shifts in the ^1H NMR on acetylation (*vide infra*), the reactions provide independent confirmation that the aryl groups of all these compounds are attached at C-2 and C-6 of the 3,7 - dioxabicyclo[3.3.0]octane nucleus.



Scheme 1.

The triol **12**, $C_{20}H_{20}O_8$, m.p. 165–7°, $[\alpha]_D$ −30°, was also isolated from the heartwood extract. The ^1H NMR spectra of the triol and its triacetate **20** (Table 4) show clearly that OH groups are attached to C-2 and C-4 (using the gummadiol numbering) since the signals at 5.23 and 6.27τ, due to H-2 and H-4 respectively, are both significantly deshielded upon acetylation. The third OH group must be attached to a quaternary centre and is clearly attached to C-1. The ^{13}C NMR spectra (Table 2) and mass spectra (Experimental) of these compounds are in complete accord with the proposed structure **12** for the triol, whilst its transformation to paulownin (Scheme 1) provides final proof of this structure.

4-Hydroxysesamin (**9**), $C_{20}H_{18}O_7$, m.p. 165°, $[\alpha]_D$ +58.4°, is an isomer of paulownin and forms a monoacetate (**21**), $C_{22}H_{20}O_8$, m.p. 100°, upon acetylation. The mass spectrum of **9** (see Table 3 and Fig. 2) contains many fragments in common with the mass spectra of gummadiol (**10**) and sesamin (**19**). In particular, the peaks at *m/e* 190, 189 and 164 all support the assignment of a 2,6 - diaryl - 3,7 - dioxabicyclo[3.3.0]octane structure,[7] rather than the alternative 2,4-diaryl-structure (see below for further comment). The peak at *m/e* 159 is clear in both the parent compound **9** and the acetate **21** (Experimental).

The ^1H NMR spectrum of 4 - hydroxysesamin **9** (Table 5) is similar to that of sesamin in that it contains two high field methine signals at 6.84 and 7.12τ. However the spectrum indicates that there is only one proton at C-4. This is seen as a doublet at 4.50τ (J = 5 Hz), coupled to the multiplet at 7.12τ, and suffers a downfield shift of 0.81 ppm upon acetylation. As both of the H-8 protons come below 6.1τ the C-2 aryl group is equatorial,[6] and since the benzylic proton at C-2 is at 5.11τ as in sesamin, the C-6 aryl group is also probably equatorial.[11] In the ^{13}C NMR spectrum of 4-hydroxysesamin **9** (Table 2), C-4 comes at 101.71 ppm as in gummadiol (101.04 ppm). The configuration of the OH group at C-4 remains however undecided, and indeed this presents a difficult problem since epimerisation at this position is very facile.

On mild oxidation with chromium trioxide in pyridine 4-hydroxysesamin (**9**) was converted into a γ-lactone (**22**) obtained as an oil ($\nu_{C=O}$ 1760 cm^{-1}). In the ^{13}C NMR spectrum of the γ-lactone the carbonyl C atom comes at 176.37 ppm. It is particularly interesting to note that a new germination inhibitor recently isolated from *Aegilops ovata* has been assigned the structure **23**[12] which may be compared with the γ-lactone (**22**) produced by oxidation of 4-hydroxysesamin. The ^1H NMR spectra of both compounds are so similar that an identical nucleus would normally be presumed. The main evidence presented in favour of the 2,4-diaryl structure for **23** was the formation of fragments of unreported relative intensity corresponding to M-84 ($ArCH\text{–}\overset{+\cdot}{O}\text{–}CHAr$) and M-85 in the mass spectrum. Indeed these fragments would be expected to be characteristic of the 2,4-diaryl series and would not be expected in the mass spectra of 2,6-diaryl compounds. However similar fragments are observed (5 and 6%) in the mass spectrum of the lactone **22** but not in the mass spectra of the parent 4-hydroxysesamin (**9**) or its acetate (**21**). By contrast these latter compounds give mass spectra in which *m/e* 164 ($ArCH\text{–}\overset{+\cdot}{O}\text{–}CH_2$), known to be characteristic of 2,6-diaryl compounds,[7] is observed as a prominent peak (10 and 12%). For this reason the fragments M-84 and M-85 in the spectra of **22** and **23** must arise by a rearrangement process. If this is so then there must be some doubt as to the correctness of the structure assigned to the germination inhibitor; in particular it is possible that it is similar to structure **22** rather than **23**.†

4,8-Dihydroxysesamin (**11**) was isolated in small quantities during the purification of gummadiol (**10**). It was separated by acetylation followed by fractional crystallisation to give the diacetate (**24**), $C_{24}H_{22}O_{10}$, m.p. 158°, $[\alpha]_D$ −30.0°. Mild acid hydrolysis then gave the dihydroxy compound **11**, $C_{20}H_{18}O_8$, m.p. 150°, $[\alpha]_D$ −14.4°, which gave a dilactone (**25**), $C_{20}H_{14}O_8$, m.p. 199°, on oxidation with chromium trioxide in pyridine. The isolation of the dilactone rather than an anhydride confirms that it is a 2,6- rather than a 2,4-diaryl compound. The mass spectrum of **11** did not show a molecular ion, or any significant peaks above *m/e* 151, but the mass spectrum of the diacetate (**24**) gave a molecular ion (see Fig. 2 and Table 3) and also prominent fragment ions at *m/e* 219, 177, 176 and 159 characteristic of compounds with an OH group at C-4.

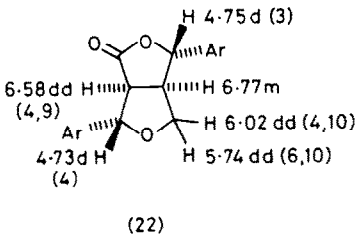
The ^1H NMR spectra (Table 6) of 4,8-dihydroxysesamin (**11**), the diacetate (**24**), and the dilactone (**25**) indicate that they are highly symmetrical molecules and are in complete accord with the assigned structures. The

†Very recently aptosimal, aptosimon and cinnamonol, compounds very similar to (**9**) and (**22**), have been assigned structure.[15,16] These structures will be commented on separately.

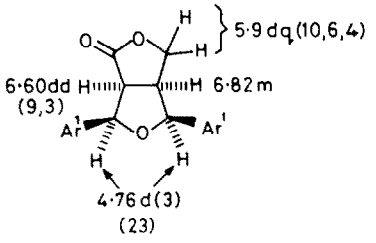
Table 5. ^1H NMR spectra of 4-hydroxysesamin and its derivatives

Proton	Sesamin (**19**) ($CDCl_3$)	4-Hydroxy-sesamin (**9**) ($CDCl_3$)	Acetate (**21**) ($CDCl_3$)	γ-Lactone (**22**) ($CDCl_3$)
1	6.95 m	6.84 m	6.85 m	6.77 m
2	5.29 d (4.5)	5.11 d (6)	5.01 d (6)	4.75 d (3)
4a	6.14 dd (4, 9)	4.50 m	3.69 br.s.	—
4e	5.77 dd (7, 9)	—	—	—
5	6.95 m	7.12 m	7.08 m	6.58 dd (4, 9)
6	5.29 d (4.5)	5.23 (6)	5.19 d (6)	4.73 d (4)
8a	6.14 dd (4, 9)	6.05 dd (2, 9)	6.05 m	6.02 dd (4, 10)
8e	5.77 dd (7, 9)	5.82 dd (6, 9)	5.80 dd (6, 10)	5.74 dd (6, 10)
OCH_2O	4.07 s	4.11 s	4.14 s, 4.15 s	4.07 s, 4.10 s
Aom.	3.1–3.3 m	2.9–3.4 m	3.0–3.4 m	3.1–3.4 m
-OH	—	—[a]	—	—
$-OCOCH_3$	—	—	8.02 s	—

[a] HO– shows at τ3.60 d (5) when spectrum run on $CDCl_3$–d_6DMSO.



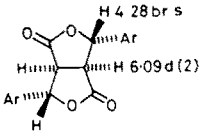
(22)



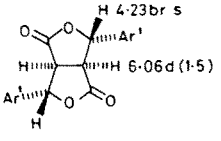
(23)

(Ar¹ = 4-hydroxy-3-methoxyphenyl)

positions of the benzylic protons would argue for all equatorial configurations of the substituents attached to the bicyclic nucleus. The protons at C-4 and C-8 appear as a doublet at 4.51τ which is shifted to 3.62τ in the spectrum of the diacetate. The spectrum of the dilactone (**25**) closely resembles that of dehydrosinapic acid dilactone (**26**), recently synthesised by Stevenson,[13] and assigned the diequatorial configuration at C-2 and C-6. It should be clear however that 4,8-dihydroxysesamin was isolated first as its diacetate which was then hydrolysed. The mechanism of hydrolysis may well involve reversible formation of stabilised carbonium ions and hence the thermodynamically most stable isomer would be formed. We have no information as to the configurations at C-4 and C-8 in the natural product itself.



(25)



(26)

(Ar¹ = 4-hydroxy-3,5-dimethoxyphenyl)

Table 6. ^{1}H NMR spectra of 4,8-dihydroxysesamin and its derivatives

Proton	4,8-Dihydroxy-sesamin (11) ($CDCl_3$-d_6DMSO)	Diacetate (24) ($CDCl_3$)	Di-γ-lactone (25) ($CDCl_3$-d_6DMSO)
1, 5	6.99dd (5, 2)	6.84dd (5, 2)	6.09d (2)
2, 6	5.15d (6)	4.93d (6)	4.28 br.s
4, 8	4.51d (4)[a]	3.62s	-
OCH_2O	4.10s	4.09s	4.04s
OCH_3	-	-	-
OH	4.1 - 4.3	-	-
$OCOCH_3$	-	7.99s	-
arom.	2.9 - 3.3m	3.1 - 3.3m	3.1 - 3.3m

[a] Becomes singlet on D_2O shake.

Table 7. ^{1}H NMR spectra of 4-O-glucoside of 4-epigummadiol and its penta-acetate

Proton	Glucoside (13) (d_6-acetone)	Penta-acetate ($CDCl_3$)
2	4.86s	4.75s
4	4.49d (4)	4.77d (3)
5	6.82dd (5, 6)	6.53dd (4, 6)
6	4.26d (6)	4.45d (6)
8a	6.19d (9)	5.68 br.s. (2H)
8e	5.95d (9)	
OCH_2O	4.10s	4.08s, 4.10s
arom.	2.9 - 3.4m	3.1 - 3.4m
OH	5.4 br., 5.95 br.s. 6.55 br. 6.88 br.	-
$OCOCH_3$	-	8.00s (6H), 8.03s (3H) 8.10s (3H), 8.28s (3H)
Sugar protons	5.4 br.d., 6.3 br. 6.55 br.	4.86m, 5.2m 5.88m, 6.3m

Finally, the glucoside (**13**), $C_{26}H_{28}O_{13}$, m.p. 95–7°, $[\alpha]_D$ +13°, was isolated as an amorphous powder which gave a penta-acetate, $C_{36}H_{38}O_{18}$, m.p. 155°, $[\alpha]_D$ +12°. Hydrolysis of **13** with cold aqueous acetone/HCl gave gummadiol (**10**) and β-D-glucose, whilst hydrolysis of the fully methylated compound gave 2,3,4,6-tetra-O-methyl glucose.

Unlike gummadiol the glucoside (**13**) did not reduce Fehling's solution, showing that the glucose unit is attached through the C-4 OH group. The ^{1}H NMR spectra of **13** and its penta-acetate (Table 7) resembled those of gummadiol (**10**) and its diacetate (**14**) and confirmed that the sugar moiety was attached to C-4 since H-4 was not moved downfield on acetylation. Interestingly the benzylic proton at C-6 of the glucoside appears as a doublet at 4.26τ (J = 6 Hz), considerably deshielded as compared to the same proton in gummadiol at 5.15τ (J = 6 Hz). This difference could indicate that the glucose residue is axially oriented so that it exerts a direct field effect on the axial proton at C-6. If so the compound would be derived from C-4-epigummadiol rather than gummadiol, hydrolysis simply giving gummadiol as the thermodynamically most stable isomer. This conclusion as to the stereochemistry at C-4 must be regarded as tentative.

In conclusion it is observed that there are notable differences in the lignan composition of the *Gmelina arborea* samples taken from Berhumpur and Vijayawada. The components of the Vijayawada samples are related to 4-hydroxysesamin (**9**) while the Berhumpur sample contains paulownin (**18**) and other related lignans. Since the woods differ so conspicuously in their composition they were sent to the Royal Botanic Gardens, Kew, for identification. In most respects the samples matched but there were "certain anatomical differences".[14] Unfortunately, due to the limited availability of samples of the genus *Gmelina*, it proved impossible for Kew to provide precise identifications.

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer 237 spectrophotometer. Mass spectra were obtained on an AEI MS9 spectrometer and NMR spectra on Varian HA100 and XL100 instruments. TLC data refer to silica gel C and the eluent stated.

Isolation of 6″ - *bromo* - *isoarboreol* (**4**). (For details of the basic extraction procedure used for the heartwood sample from Berhampur, see Ref. 1).

Fractions 71–80 on concentration and fractional crystallisation gave (+)-paulownin (500 mg), R_f 0.53 (benzene–ethyl acetate, 9:1), and arboreol (400 mg), R_f 0.25. The mother liquor showed two more spots, R_f 0.45 and 0.33, in addition to those of paulownin and arboreol. They could not be separated by fractional crystallisation but were partially separated by preparative thin layer chromatography using 12 plates (20 × 20 cm) coated with silica gel C and the above solvent system. Three bands were separated:

Band I—Contained (+)-paulownin.

Band II—Contained paulownin and the compound having R_f 0.45 as minor components and the compound having R_f 0.33 as major component.

Band III—Contained arboreol.

Fractional crystallisation of band II (200 mg) was unsuccessful so it was adsorbed on silica gel (450 mg) (100–200 mesh), placed on a column of silica gel (1 ft × 0.25 in) and eluted with hexane–benzene (7:3). Fractions (15 ml) were collected and those having R_f 0.33 were combined. Two crystallisatisations from methanol gave 6″ - bromo - isoarboreol (150 mg) as colourless crystals, m.p. 190°, $[\alpha]_D$ −22.5°, ν_{max}^{Nujol} 3400, 1600, 935, 875, 840 and 815 cm^{-1}. (Found: C, 51.43; H, 3.80. $C_{20}H_{17}BrO_8$ requires C, 51.60; H, 3.66%).

The remaining fractions contained the compound having R_f 0.45 but this was found to be unstable.

Periodate oxidation of 6″ - *bromo* - *isoarboreol* (**4**). 6″ - Bromo - isoarboreol (70 mg) was dissolved in dioxan (8 ml) and an aqueous soln of potassium periodate (70 mg in 4 ml) was added. The reaction was complete in 10 hr at room temp. (change in R_f from 0.33 to 0.73, benzene-ethyl acetate 9:1). The mixture was poured into water (150 ml) and thoroughly extracted with ether. The ether layer was washed with dil aq $NaHCO_3$ and water, dried ($MgSO_4$), filtered and evaporated. Crystallisation of the residue from benzene–hexane gave **5** as colourless prisms (50 mg), m.p. 122°, R_f 0.73. (Found: C, 51.65; H, 3.20. $C_{20}H_{15}BrO_8$ requires: C, 51.72; H, 3.23%); ν_{max}^{Nujol} 1760 (5-membered ketone), 1720 (arom. ester), 1600, 935, 830 and 815 cm^{-1}. *M/e* 298 (23), 296 (24), 240 (13), 238 (13), 229 (18), 227 (18), 187 (16), 166 (100), 165 (89), 160 (11), 159 (27), 149 (51), 121 (11). In acidic solution the reaction was complete in 40 min and the same keto-ester obtained.

Alkaline hydrolysis of the keto-ester (**5**). A soln of the keto-ester (50 mg) in 4% methanolic alkali (10 ml) was refluxed for 0.5 hr. The MeOH was removed under reduced pressure and the remainder extracted with ether. Evaporation of the ether layer gave a colourless solid (25 mg), m.p. 244–6°, (3 spots), which could not be separated. It gave a positive Beilstein test for the presence of bromine. ν_{max}^{Nujol} 3480 br (OH), 1760 (5-membered ketone), 1600, 935 and 815 cm^{-1}. The alkaline layer was acidified with dil. HCl and extracted with ether. Evaporation of the dried ether extract gave a solid which crystallised from benzene as colourless needles (15 mg), m.p. 225–7°, undepressed by admixture with an authentic sample of piperonylic acid.

Bromination of 2-O-*methyl arboreol* (**7**)

Formation of 6″ - *bromo* - *arboreol* (**8**). To a soln of 2 - O - methyl arboreol (200 mg) in dry chloroform (5 ml), a soln of Br_2 (0.05 ml) in dry chloroform (2 ml) was added dropwise with stirring. The mixture was kept at room temp. for about 20 min. The solid which separated was filtered and recrystallised from MeOH to give **8** as colourless needles (100 mg), m.p. 164°, $[\alpha]_D$ −6°, R_f 0.33 (benzene–ethyl acetate 9:1). (Found: C, 51.64; H, 3.70. $C_{20}H_{17}BrO_8$ requires: C, 51.60; H, 3.66%); ν_{max}^{Nujol} 3400 (OH), 1600 (arom.), 935 (OCH_2O), 875, 840 and 815 (C–Br) cm^{-1}. (Found: M^+ 464.0107/466.0088. $C_{20}H_{17}BrO_8$ requires: 464.0107/466.0088). Accurate mass measurements: *m/e* 446.0002/467.9982 ($C_{20}H_{15}BrO_7$), 415.9896/417.9876 ($C_{19}H_{13}BrO_6$), 336.0634 ($C_{19}H_{12}O_6$), 238.9708/240.9686 ($C_{10}H_8BrO_2$).

Periodate oxidation of 6″ - *bromo* - *arboreol* (**8**). 6″ - Bromo - arboreol (100 mg) was dissolved in dioxan (10 ml) and an aqueous soln of potassium periodate (100 mg in 5 ml) was added. The reaction was complete in 4.5 hr at room temp. (change in R_f from 0.33 to 0.73). The product was identical to **5** obtained from 6″ - bromo - isoarboreol (IR and mmp).

Isomerisation of 6″ - *bromo* - *arboreol* (**8**)

Formation of 6″ - *bromo* - *isoarboreol* (**4**). 6″ - Bromo - arboreol (80 mg) in aqueous acetone (1:1, 10 ml) was treated with conc HCl (5 drops) and left at room temp. for 2 hr. On concentration **4** crystallised out as colourless needles (70 mg), m.p. 190° $[\alpha]_D$ −22.5°, R_f 0.33 (Found: C, 51.65; H, 3.72. $C_{20}H_{17}O_8Br$ requires: C, 51.60; H, 3.66%); ν_{max}^{Nujol} 3400, 1610, 935, 840 and 815 cm^{-1}.

Bromination of 2 - O - *methyl isoarboreol* (**6**)

Formation of 6″ - *bromo* - *isoarboreol* (**4**). A soln of Br_2 in dry chloroform (0.05 ml in 2 ml) was added to 2 - O - methyl - isoarboreol (100 mg) in dry chloroform (5 ml) dropwise with constant stirring. After 15 min the solid which separated was filtered and crystallised from MeOH to give **4** as colourless crystalline needles, m.p. 190°, $[\alpha]_D$ −22.5°, identical in all respects to the naturally occurring compound.

Extraction of the heartwood of Gmelina arborea *Linn. from Vijayawada*

The powdered *G. arborea* Linn. heartwood (4 kg) from Vijayawada, Andhra Pradesh, was extracted thoroughly with methylated spirit in a large Soxhlet extractor. The solvent was completely removed under reduced pressure and the residue adsorbed on spent powder. It was then fractionated successively with n-hexane, EtOAc, and methanol in a soxhlet extractor.

The yellow n-hexane extract contained only waxy material and was not investigated further.

The dark-brown coloured EtOAc extract was concentrated to 1 litre and washed thoroughly with 5% NaOH aq to take out the phenols. The EtOAc layer did not yield any crystalline material on concentration, but showed 8 distinct spots on TLC (benzene : ethyl acetate, 7 : 3). The gummy residue (30 g) was adsorbed on silica gel (90 g, 100–200 mesh) and the dry powder placed on to a column (3 ft × 2.5 in.) of silica gel under n-hexane. The fractions (1 l.) were monitored by TLC and combined where appropriate. The results are shown in Table 8.

Fractions 1–5 yielded only a small amount of oil (150 mg) which was not examined further.

The products from fractions 6–15 were combined and recrystallised from benzene–hexane when compound A was obtained as colourless needles, m.p. 86° (280 mg). Fractions 18–23 yielded pure compound B, m.p. 134° (100 mg). Fractions 16–17 and 24–27 were combined and crystallised from MeOH when more of compound B (50 mg) was obtained as colourless plates. The residue, on further crystallisation, from benzene–hexane deposited some more compound A (20 mg). Pure compound C crystallised from fractions 28–33 as colourless needles (170 mg) m.p. 165° from benzene.

The solvent from fractions 34–40 was removed under vacuum, the residue dissolved in a minimum amount of acetone and applied on 20 plates (20 × 20 cm) coated with silica gel C. The plates were developed with benzene–EtOAc (9 : 1). Two bands were visible under UV light and were separated. The material obtained from band I was crystallised from benzene to give compound C (30 mg) and band II gave compound D (850 mg). Fractions 41–60 yielded only compound D (22.8 g) which on recrystallisation from ethyl acetate–benzene came out as colourless needles, m.p. 130°.

Fractions 61–65 showed two close spots on TLC. As it could not be fractionally crystallised, the solid (850 mg) was adsorbed on silica gel (3 g) and eluted with benzene, 50 ml fractions being collected. The first 15 fractions gave compound D (400 mg). The next 20 fractions gave a mixture of two components (430 mg) with very close R_f values. Further elution of the column with benzene–EtOAc (9 : 1) gave 20 mg of a compound F, which crystallised from EtOAc as colourless buttons, m.p. 158°. As fractional crystallisation failed to separate the above mixture, it was acetylated and then crystallised from MeOH. The first crop of colourless needles was found to be the acetate of the compound E (200 mg). The filtrate on further crystallisation gave the acetate of compound D as colourless needles (250 mg).

Fractions 66–68 gave more of the pure compound F (15 mg).

Compound G was obtained from fractions 69–74 and crystallised as colourless plates from MeOH, m.p. 165–7° (200 mg).

Removal of solvent from fractions 75–85 gave a brown gum which resisted crystallisation, but further chromatography on an alumina column (1.5 ft × 0.75 in.) using $CHCl_3$–CH_3OH (9 : 1) gave compound H as a colourless gum (1 g).

Identification of compound A

3,4-*Methylenedioxycinnamaldehyde.* Compound A crystallised from benzene–hexane as colourless needles, m.p. 86°. This was found to be identical (m.m.p. and IR) with an authentic sample. (Found: C, 68.15; H, 4.45. $C_{10}H_8O_3$ requires: C, 68.18; H, 4.58%); ν_{max}^{Nujol} 1670, 1640, 1600 and 930 cm^{-1}.

Identification of compound B

β-*Sitosterol.* Compound B crystallised from MeOH as colourless flakes, m.p. 134°, $[\alpha]_D$ −37°, m.p. undepressed with an authentic sample of β-sitosterol.

Examination of compound C

4-*Hydroxysesamin* (**9**). Compound C crystallised from benzene as colourless needles, m.p. 165°, $[\alpha]_D$ +58.4°, R_f 0.85 (benzene–EtOAc 7 : 3). (Found: C, 64.72; H, 5.11. $C_{20}H_{18}O_7$ requires: C, 64.86; H, 4.9%); (Found: M^+ 370.1053. $C_{20}H_{18}O_7$ requires: 370.1053); ν_{max}^{Nujol} 3350 (OH), 1600 (arom.) and 935 (OCH_2O) cm^{-1}. Accurate mass measurements: *m/e* 368.0896 ($C_{20}H_{16}O_7$), 202.0631 ($C_{12}H_{10}O_3$).

Acetate (**21**) *of* 4-*hydroxysesamin.* The acetate (Ac_2O + pyridine at 100° for 5 hr) of **9** crystallised from MeOH as colourless needles, m.p. 100°, R_f 0.6 (benzene–EtOAc 9 : 1). (Found: C, 64.0; H, 4.9. $C_{22}H_{20}O_8$ requires: C, 64.08; H, 4.89%); (Found: M^+ 412.1158. $C_{22}H_{20}O_8$ requires: 412.1158); ν_{max}^{Nujol} 1740 (AcO), 1600 (arom), and 935 (OCH_2O) cm^{-1}. *m/e* 412 (12), 370 (13), 352 (12), 323 (19), 203 (35), 202 (30), 189 (24), 177 (12), 176 (19), 174 (12), 173 (24), 164 (12), 162 (12), 161 (69), 159 (10), 151 (67), 150 (30), 149 (100), 148 (10), 136 (10), 135 (83), 131 (53), 122 (17), 121 (16). Accurate mass measurements: *m/e* 189.0551 ($C_{11}H_9O_3$).

γ-*Lactone* (**22**) *from* 4-*hydroxysesamin.* To a soln of 4-hydroxysesamin (20 mg) in pyridine (2 ml) was added CrO_3 (20 mg) and the mixture kept at room temp. Work-up in the usual way gave the γ-lactone as an oily product, R_f 0.65 (benzene–EtOAc 9 : 1). (Found: C, 66.4; H, 4.20. $C_{20}H_{16}O_7$ requires: C, 66.22; H, 4.38%); (Found: 368.0893. $C_{20}H_{16}O_7$ requires: 368.0896). ν_{max}^{film} 1760 (lactone), 1600 (arom) and 935 (OCH_2O) cm^{-1}; *m/e* 368 (79), 284 (5), 283 (6), 255 (7), 173 (7), 163 (6), 162 (5), 161 (44), 151 (7), 150 (37), 149 (100), 148 (10), 135 (40), 131 (59), 121 (12), 116 (10), 103 (16).

Table 8.

Fraction No.	Eluent	Compounds present	Yield
1-5	Hexane	Oil	150 mg
6-15	Hexane	A	280 mg
16-17	Hexane:Benzene (8:2)	A and B	20 mg
18-23	Hexane:Benzene (8:2)	B	100 mg
24-27	Hexane:Benzene (1:1)	A, B and C	85 mg
28-33	Hexane:Benzene (1:1)	C	170 mg
34-40	Benzene	C and D	880 mg
41-60	Benzene	D	22.8 g
61-65	Benzene:EtOAc (8:1)	D, E and F	850 mg
66-68	Benzene:EtOAc (8:2)	F	15 mg
69-74	Benzene:EtOAc (6:4)	G	200 mg
75-85	EtOAc	H	1 g

Examination of compound D

Gummadiol (**10**). Compound D crystallised from EtOAc–benzene as colourless needles, m.p. 130°, $[\alpha]_D$ +32°, R_f 0.58 (benzene–EtOAc 7:3). (Found: C, 62.75; H, 4.98. $C_{20}H_{18}O_8$ requires: C, 62.18; H, 4.70%). (Found: M^+ 386.1003. $C_{20}H_{18}O_8$ requires: 386.1003); ν_{max}^{Nujol} 3580 (OH), 3400 (OH), 1600 (arom.), and 935 (OCH_2O) cm^{-1}. Accurate mass measurements: *m/e* 370.1054 ($C_{20}H_{18}O_7$), 368.0897 ($C_{20}H_{16}O_7$), 350.0791 ($C_{20}H_{14}O_6$), 338.0791 ($C_{19}H_{14}O_6$), 210.0529 ($C_{10}H_{10}O_3$), 192.0421 ($C_{10}H_8O_4$), 176.0474 ($C_{10}H_8O_3$), 151.0396 ($C_8H_7O_3$), 149.0239 ($C_8H_5O_3$).

Gummadiol diacetate (**14**). The acetate (Ac_2O-pyridine, 100° for 2 hr) crystallised as colourless needles from MeOH, m.p. 140°, $[\alpha]_D$ +31°, R_f 0.64 (benzene–EtOAc 9:1). (Found: C, 61.3; H, 4.65. $C_{24}H_{22}O_{10}$ requires: C, 61.28; H, 4.71%); (Found: M^+ 470.1215. $C_{24}H_{22}O_{10}$ requires: 470.1215). ν_{max}^{Nujol} 1740 (AcO), 1600 (arom), and 935 (OCH_2O) cm^{-1} *m/e* 470 (22), 350 (22), 260 (24), 218 (27), 205 (21), 201 (22), 177 (19), 159 (9), 152 (10), 151 (100), 150 (12), 149 (30), 135 (14). Accurate mass measurements: *m/e* 350.0792 ($C_{20}H_{14}O_6$), 260.0685 ($C_{14}H_{12}O_5$), 235.0607 ($C_{12}H_{11}O_5$), 218.0579 ($C_{12}H_{10}O_4$), 205.0506 ($C_{11}H_9O_4$), 201.0555 ($C_{12}H_9O_3$).

CrO_3–AcOH *Oxidation of gummadiol* (**10**). Gummadiol (100 mg) was dissolved in glacial AcOH (2 ml) and to this CrO_3 (100 mg) was added. After keeping the mixture overnight at room temp., a few drops of MeOH were added to destroy the excess CrO_3, the mixture diluted with water and extracted with EtOAc. The organic layer was washed with water, dried ($MgSO_4$), and evaporated to give a colourless solid, which afforded colourless needles from benzene (60 mg), m.p. 225°, undepressed by mixing with an authentic sample of piperonylic acid.

γ-Lactone (**15**) *from gummadiol.* To a soln of gummadiol (500 mg) in pyridine (15 ml), CrO_3 (350 mg) was added and the mixture kept at room temp. overnight. The mixture was poured into water and worked-up as usual. The γ-lactone crystallised from MeOH as colourless needles (300 mg), m.p. 157°, $[\alpha]_D$ +43.3°, R_f 0.57 (benzene–EtOAc 8:2). (Found: C, 62.3; H, 4.25. $C_{20}H_{16}O_8$ requires: C, 62.50; H, 4.2%). (Found: M^+ 384.0845. $C_{20}H_{16}O_8$ requires: 384.0845); ν_{max}^{Nujol} 3500 (OH), 1770 (γ-lactone), 1600 (arom), and 935 (OCH_2O) cm^{-1}; *m/e* 384 (100), 206 (29), 205 (51), 192 (6), 177 (12), 176 (13), 175 (14), 164 (6), 163 (5), 151 (24), 150 (23), 149 (60), 148 (43), 147 (22), 135 (26).

LAH *reduction of γ-lactone* (**15**). The γ-lactone **15** (250 mg) in anhyd THF (20 ml) was added to a slurry of LAH (150 mg) in anhyd THF (10 ml) and refluxed for 4 hr. After the usual work-up the product (**12**) crystallised from MeOH as colourless needles (150 mg), m.p. 165–7°, $[\alpha]_D$ −29.5°, R_f 0.56 (benzene–EtOAc 1:1). (Found: C, 61.4; H, 5.15. $C_{20}H_{20}O_8$ requires: C, 61.85; H, 5.19%); ν_{max}^{Nujol} 3530 (OH), 3480 (OH), 3360 (OH), 1600 (arom.), and 920 (OCH_2O) cm^{-1}.

Reduction of gummadiol (**10**) *with* LAH *and* $AlCl_3$. Gummadiol (100 mg) in anhyd THF (10 ml) was refluxed with LAH (50 mg) and $AlCl_3$ (15 mg) for 5 hr. Excess LAH was destroyed by ice-cold water and the residue extracted with EtOAc. The EtOAc layer was washed with water, dried ($MgSO_4$) and evaporated to give the triol (40 mg) which crystallised from MeOH as colourless plates, m.p. 165–7°, and was identical in all respects with the triol obtained by reduction of gummadiol γ-lactone, and with the product isolated from the wood (compound G).

Reduction of arboreol (**1**) *with* LAH *and* $AlCl_3$. Arboreol (100 mg) in anhyd THF (10 ml) was refluxed with LAH (60 mg) and $AlCl_3$ (15 mg) for 5 hr. After working-up in the usual way, the product obtained was identical by m.m.p. and IR with **12**.

Triacetate (**20**) *of triol* **12**. The acetate (Ac_2O-pyridine, 100° for 2 hr) was obtained as an oily product, R_f 0.67 (benzene–EtOAc 8:2). (Found: C, 60.67; H, 5.12. $C_{26}H_{26}O_{11}$ requires: C, 60.70; H, 5.0%); ν_{max}^{Nujol} 1735 (AcO), 1600 (arom.), and 935 (OCH_2O) cm^{-1}; (Found: M^+ 514.1470. $C_{26}H_{26}O_{11}$ requires: 514.1475). Accurate mass measurements: *m/e* 220.0736 ($C_{12}H_{12}O_4$), 202.0628 ($C_{12}H_{10}O_3$).

Conversion of triol (**12**) *into paulownin* (**18**). The triol (100 mg) was dissolved in MeOH (20 ml) saturated with HCl, and refluxed for 3 hr. The mixture was diluted with water and extracted with EtOAc. The EtOAc layer was washed with water, $NaHCO_3$ aq, dried ($MgSO_4$) and evaporated to give a brown residue which on passing through silica gel and crystallisation from MeOH gave colourless crystals (50 mg), m.p. 105°, $[\alpha]_D$ +29°, R_f 0.53 (benzene–EtOAc 9:1). (Found: C, 64.60; H, 5.10. $C_{20}H_{18}O_7$ requires: C, 64.86; H, 4.9%). The product was identical with an authentic sample of (+)-paulownin (**18**) by m.m.p. and IR.

Axial 4 - O - *methyl ether of gummadiol* (**16**). Gummadiol (100 mg) in MeOH (10 ml) was treated with 2 drops of conc HCl and left for 2 hr at room temp. The mixture was poured into water and the product crystallised from MeOH to give colourless needles (80 mg), m.p. 176°, $[\alpha]_D$ −22.5°, R_f 0.48 (benzene–EtOAc 9:1). (Found: C, 63.2; H, 5.01. $C_{21}H_{20}O_8$ requires: C, 63.0; H, 5.03%); (Found: M^+ 400.1158. $C_{21}H_{20}O_8$ requires: 400.1158); ν_{max}^{Nujol} 3420 (OH), 2830 (OMe), 1610 (arom.), and 930 (OCH_2O) cm^{-1}. *m/e* 400 (32), 218 (10), 192 (12), 191 (91), 151 (64), 150 (12), 149 (17), 148 (12), 135 (14).

Equatorial 4 - O - *methyl ether of gummadiol* (**17**). Gummadiol (100 mg) in MeOH (15 ml) was treated with 4 drops of conc HCl and refluxed on a water bath for 2 hr. The product upon crystallisation from MeOH gave colourless needles (75 mg), m.p. 182°, $[\alpha]_D$ +36°, R_f 0.48, different from **16**; m.m.p. 152°. (Found: C, 62.5; H, 5.08. $C_{21}H_{20}O_8$ requires: C, 63.0; H, 5.03%); (Found: M^+ 400.1158. $C_{21}H_{20}O_8$ requires: 400.1158); ν_{max}^{Nujol} 3420 (OH), 2830 (OMe), 1610 (arom.), and 930 (OCH_2O) cm^{-1}; *m/e* 400 (29), 218 (9), 192 (13), 191 (91), 151 (63), 150 (11), 149 (16), 148 (11), 135 (14).

Examination of compound E acetate

Diacetate (**24**) *of* 4,8-*dihydroxysesamin.* The acetate **24** of compound E was separated by fractional crystallisation of the acetate mixture of D and E, and recrystallised from MeOH as colourless needles, m.p. 158°, $[\alpha]_D$ −30°, R_f 0.82 (benzene–EtOAc 9:1). (Found: C, 61.24; H, 4.75. $C_{24}H_{22}O_{10}$ requires: C, 61.28; H, 4.7%); (Found: M^+ 470.1213. $C_{24}H_{22}O_{10}$ requires: 470.1213). ν_{max}^{Nujol} 1730 (AcO), 1600 (arom), and 930 (OCH_2O) cm^{-1}. Accurate mass measurements: *m/e* 219.0657 ($C_{12}H_{11}O_4$), 176.0473 ($C_{10}H_8O_3$), 159.0441 ($C_{10}H_7O_2$).

Hydrolysis of compound E acetate

Isolation of 4,8-*dihydroxysesamin* (**11**). The acetate **24** (120 mg) was dissolved in aqueous acetone (15 ml, 1:1) and 5 drops of conc HCl added. After 4 hr at room temp. colourless needles separated and were filtered off. The solid was recrystallised from benzene to give **11** as needles (90 mg), m.p. 150°, $[\alpha]_D$ −14.4°, R_f 0.58 (benzene–EtOAc 7:3). (Found: C, 62.27; H, 4.67. $C_{20}H_{18}O_8$ requires: C, 62.18; H, 4.70%); ν_{max}^{Nujol} 3250 (OH), 1600 (arom), and 925 (OCH_2O) cm^{-1}.

Di - γ - lactone (**25**) *from* 4,8 - *dihydroxysesamin.* 4,8 - Dihydroxysesamin (75 mg) in pyridine (5 ml) was treated with CrO_3 (45 mg) and the mixture kept at room temp. for 18 hr. After the usual work-up **25** crystallised from MeOH as colourless prisms (50 mg), m.p. 199°, R_f 0.86 (benzene–EtOAc 8:2). (Found: C, 62.77; H, 3.72. $C_{20}H_{14}O_8$ requires: C, 62.83; H, 3.69%); ν_{max}^{Nujol} 1760 (lactone), 1610 (arom), and 930 (OCH_2O) cm^{-1} *m/e* 382 (78), 188 (47), 175 (12), 150 (27), 149 (100), 135 (14), 122 (11), 121 (10).

Examination of compound G

2 - (3,4 - *Methylenedioxyphenyl*) - 3 - *hydroxy* - *methyl* - 4 - (α - *hydroxy* - 3,4 - *methylenedioxybenzyl*) - 4 - *hydroxytetrahydrofuran* (*Triol* **12**). Compound G crystallised from MeOH as colourless needles, m.p. 165–7°, $[\alpha]_D$ −30°, R_f 0.56 (benzene–EtOAc 1:1). It was identical with **12** obtained from gummadiol by m.m.p. and IR. (Found: M^+ 388.1158. $C_{20}H_{20}O_8$ requires: 388.1158); *m/e* 388 (1), 370 (18), 238 (11), 220 (22), 205 (13), 163 (12), 161 (15), 152 (46), 151 (100), 150 (32), 149 (31), 148 (11), 135 (33), 131 (15), 122 (11). Accurate mass measurement: *m/e* 370.1053 ($C_{20}H_{18}O_7$).

Triacetate (**20**) *of triol* **12**. The oily product (Ac_2O-pyridine, 100° for 4 hr) obtained was identical in all respects with the acetate of **12** from gummadiol (TLC and IR). *m/e* 514 (15), 394 (22), 335 (31), 334 (13), 219 (12), 203 (14), 202 (43), 193 (26), 186 (19), 161 (14), 152 (22), 151 (100), 150 (24), 149 (87), 135 (33), 131 (15), 122 (13), 121 (13).

Examination of compound H

4 - *Epigummadiol* - 4 - O - β - D - *glucoside* (**13**). Compound H was obtained as a colourless gum which solidified to an amorphous powder after leaving for a few hr in vacuum, m.p.

95–7°, $[\alpha]_D$ +13°. (Found: C, 56.7; H, 5.08. $C_{26}H_{28}O_{13}$ requires: C, 56.94; H, 5.07%); ν_{max}^{Nujol} 3380 (OH), 1600 (arom), and 925 (OCH_2O) cm^{-1}.

Pentaacetate of compound H. The acetate (Ac_2O-pyridine, 100° for 6 hr) crystallised from MeOH as colourless buttons, m.p. 155°, $[\alpha]_D$ +12°. (Found: C, 56.85; H, 4.9. $C_{36}H_{38}O_{18}$ requires: C, 56.99; H, 5.01%); (Found: M$^+$ 758.2058. $C_{36}H_{38}O_{18}$ requires: 758.2058); ν_{max}^{Nujol} 1745 (OAc), 1600 (arom), and 935 (OCH_2O) cm^{-1}; *m/e* 758 (2), 351 (49), 350 (100), 331 (22), 322 (11), 321 (19), 202 (29), 201 (100), 177 (12), 169 (91), 159 (8), 151 (41), 150 (18), 149 (68), 148 (13), 145 (12), 135 (25), 127 (21), 115 (22), 109 (66), 103 (11). Accurate mass measurements: *m/e* 350.0790 ($C_{20}H_{14}O_6$), 331.1029 ($C_{14}H_{19}O_9$), 201.0552 ($C_{12}H_9O_3$), 169.0501 ($C_8H_9O_4$).

Hydrolysis of compound H (**13**). Compound H (100 mg) in aqueous acetone (10 ml, 1:1) was treated with 4 drops of conc HCl and left for 4 hr at room temp. The aglycone was removed by extraction with ether (3 × 15 ml). The product obtained after evaporation of ether and recrystallisation from EtOAc–benzene gave colourless needles of gummadiol identical with an authentic sample by TLC, m.m.p. and IR. The filtrate after neutralisation with $BaCO_3$ was concentrated to 1 ml under reduced pressure at 50°. Ascending and circular chromatograms on Whatman No. 1 filter paper were obtained using BuOH–AcOH–water (4:1:5). The spray reagent was aniline hydrogen phthalate. The R_f values are shown below and compared with those of an authentic sample of D-glucose run under the same conditions.

	Ascending	Circular
Sugar in hydrolysate	0.28	0.31
Authentic sugar	0.28	0.31

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