A Natural Phenolic Lignan From *Tinospora cordifolia* Miers

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Systematic chemical investigation of *Tinospora cordifolia* Miers has yielded a new phenolic lignan along with the known compounds octacosanol, nonacosan-15-one, and β-sitosterol. This lignan has been shown by a combination of spectroscopic and chemical methods to be 3-(α,4-dihydroxy-3-methoxybenzyl)-4-(4-hydroxy-3-methoxybenzyl)tetrahydrofuran (**1**)

Tinospora cordifolia Miers, Locally know as 'Guduchi,' belongs to the family *Menispermaceae* and is distributed throughout India. This plant is well known in Ayurvedic medicine and has been found to exhibit pharmacological properties in animal tests;[1] earlier, the furano-diterpenes[2–4] tinosporin, tinosporide, and cordifolide which are related to colubin[5] have been isolated from it. Our interest in indigenous medicinal plants led us to study this plant and a hot chloroform extract of the stems yielded a new phenolic lignan along with the known compounds octacosanol, nonacosan-15-one, and β-sitosterol. Although the biological activity of this lignan has yet to be evaluated, other tetrahydrofuran lignans have been shown to act both as CNS stimulants and synergistically with the insecticide pyrethrum.[6–8]

Elemental and mass spectral analysis (M^+, 360) suggested the molecular formula $C_{20}H_{24}O_6$ for compound (**1**). Its u.v. [$\lambda_{max.}$(MeOH) 232.5 and 285.0 nm (ε 11 000 and 16 000)] and i.r. ($\nu_{max.}$ 3 500, 3 470, 3 370, 1 615, and 1 520 cm^{-1}) data suggested an aromatic nature and the presence of hydroxy groups. It showed bands at 1 270, 1 240, and 1 210 cm^{-1} for the presence of an aromatic ether, and the presence of an aliphatic ether linkage was also indicated (980, 940 cm^{-1}). The presence of a phenolic hydroxy group was suggested by a positive ferric chloride test (green colouration) and the development of a pink colour over the t.l.c. plate on spraying with the Folin-Ciocalteu reagent.

The 100 MHz ^{1}H n.m.r. spectrum showed signals corresponding to 24 protons and had the general features of tetrahydrofuran lignans (Table 3).[9,10] The complex nature of several signals necessitated the recording of the ^{1}H n.m.r. spectrum on a high resolution instrument (500 MHz).

The ^{1}H n.m.r. spectrum of (**1**) (Table 1) ($CDCl_3$) showed a quintet at δ 2.40, double doublets at 2.55, and 2.91, and one multiplet at 2.73, which were attributed to 8′-H, 7-H_A, 7-H_B, and 8-H, respectively. Four double doublets were observed at δ 3.74, 3.84, 3.91, and 4.05, which were assigned to 9-H_A, 9′-H_A, 9′-H_B, and 9-H_B, respectively. There were two singlets at δ 3.87 and 3.88, for two methoxy groups, and one doublet at δ 4.77, assigned to 7′-H. Two D_2O exchangeable singlets at δ 5.49 (1 H) and 5.57 (1 H) were attributed to phenolic protons. The aro-

Table 1. ^{1}H N.m.r. data of compound (**1**) and its derivatives

Proton	(1)[b]	(1a)[d]	(1b)[c]	(1c)[b]	(1d)[d]	(1e)[d]
2-H	6.68 (s)	6.62 (br s)	6.73 (d, *J* 1.8)	6.59 (d, *J* 1.5)		6.62—6.78 (m)
2′-H	6.86 (s)	6.65 (s)	6.75 (d, *J* 1.8)	6.28 (s)		6.42 (s)
5-H	6.86 (d, *J* 8.0)	6.80 (d, *J* 8.0)	6.95 (d, *J* 8.0)	6.83 (d, *J* 8.0)		7.00 (d, *J* 8.0)
5′-H	6.90 (d, *J* 8.0)	6.63 (s)	6.99 (d, *J* 8.0)	6.57 (s)	6.18–6.82(m)	
6-H	6.68 (dd, *J* 2.0, 8.0)	6.54 (dd, *J* 2.0, 8.0)	6.86 (dd, *J* 1.7, 8.0)	6.64 (dd, *J* 1.6, 8.0)		6.62—6.78 (m)
6′-H	6.81 (dd, *J* 2.0, 8.0)		6.87 (dd, *J* 1.6, 8.0)			
7-H_A	2.55 (dd, *J* 5.4, 13.6)	2.5—3.0 (m)	2.57 (m)	2.74 (dd, *J* 4.6, 15.8)	2.15 (m)	2.88 (br d)
7-H_B	2.91 (dd, *J* 5.2, 13.2)		2.86 (dd, *J* 8.0, 13.0)	2.81 (dd, *J* 4.3, 15.8)		
7′-H	4.77 (d, *J* 6.6)	6.24 (s)	4.85 (d, *J* 5.5)	3.71 (d, *J* 6.7)		3.90—4.22 (m)
8-H	2.73 (m)		2.87 (m)	2.02 (m)	1.50—1.80 (m)	1.90—2.34 (m)
8′-H	2.40 (quintet, *J* 6.8, 13.7)	[a]	2.55 (m)	1.84 (m)	2.50—2.80 (m)	
9-H_A	3.74 (dd, *J* 6.4, 8.5)	3.34—4.18 (m)	4.09 (m)	3.77 (dd, *J* 3.0, 10.0)		
9-H_B	4.05 (dd, *J* 6.5, 8.5)		4.21 (dd, *J* 7.0, 11.0)	3.87 (dd, *J* 3.0, 10.0)	3.80—4.40 (m)	3.90—4.22 (m)
9′-H_A	3.84 (dd, *J* 6.1, 10.5)		3.86 (m)	3.71 (dd, *J* 5.5, 10.5)		
9′-H_B	3.91 (dd, *J* 6.6, 10.6)		4.37 (dd, *J* 6.6, 11.0)	3.51 (dd, *J* 5.0, 10.0)		
3-OMe	3.87 (s)		3.81 (s)	3.82 (s)	3.76 (s)	3.78 (s)
3′-OMe	3.88 (s)		3.83 (s)	3.85 (s)	3.94 (s)	3.82 (s)
4-OH	5.49 (s)	7.56, 7.74 (each br s)		5.32 (s)	5.58—5.66 (br s)	
4′-OH	5.57 (s)			5.52 (s)		
7-OH				1.60 (br s)		
9-OH						
4-OAc			2.30 (s)			2.22 (s)
4′-OAc						2.32 (s)
7′-OAc			2.04 (s)			2.06 (s)
9-OAc						

[a] No signal was observed for 8′-H. [b] 500 MHz, $CDCl_3$. [c] 250 MHz, $CDCl_3$. [d] 100 MHz, CD_3COCD_3, $CDCl_3$; TMS as internal standard, coupling constants (*J*) in Hz; assignments were made by decoupling studies.

Table 2. ^{13}C N.m.r. data for compounds (1), (1b), and (1c)[a]

Carbon	(1)	(1b)	(1c)
1	133.47 (s)	138.89 (s)	138.18 (s)
2	113.11 (d)	112.80 (d)	111.70 (d)
3	148.32 (s)	151.13 (s)	147.97 (s)
4	145.74 (s)	139.10 (s)	146.13 (s)
5	116.28 (d)	120.55 (d)	115.24 (d)
6	121.89 (d)	122.79 (d)	122.70 (d)
7	34.01 (t)	33.44 (t)	33.60 (t)
8	43.52 (d)	42.11 (d)	47.61 (d)
9	73.71 (t)	72.38 (t)	65.90 (t)
1′	136.67 (s)	138.35 (s)	133.69 (s)
2′	110.38 (d)	109.72 (d)	114.92 (d)
3′	148.20 (s)	151.13 (s)	144.93 (s)
4′	146 53 (s)	141.51 (s)	145.23 (s)
5′	114.86 (d)	117.76 (d)	117.51 (d)
6′	119.32 (d)	122.61 (d)	128.21 (s)
7′	83.70 (s)	82.82 (d)	82.00 (d)
8′	53.93 (d)	49.04 (d)	40.31 (d)
9′	61.03 (t)	62.64 (t)	62.10 (t)
OMe	57.47 (2q)	55.89 (2q)	55.88 (2q)
OCO*Me*		20.91 (3q)	
O*CO*Me		169.03 (2s)	
		170.86 (s)	

[a] Run at 65.2 MHz in $CDCl_3$ with TMS as an internal standard.

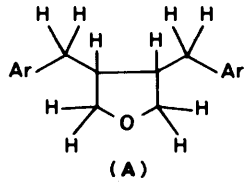
Table 3. ^1H N.m.r. data of tetrahydrofuran lignans[10]

Proton	Carissanol	(+)-Laricresinol	(−) Olivil
2-H	7.07—6.57	6.95 (d, *J* 2.0)	7.14 (d, *J* 2.0)
2′-H		6.84 (d, *J* 2.0)	6.96 (d, *J* 2.0)
5-H		6.80 (d, *J* 8.0)	6.73 (d, *J* 8.0)
5′-H		6.75 (d, *J* 8.0)	6.75 (d, *J* 8.0)
6-H		6.75 (dd, J_1 8.0, J_2 2.0)	6.88 (dd, J_1 8.0, J_2 2.0)
6′-H		6.66 (dd, J_1 8.0, J_2 2.0)	6.77 (dd, J_1 8.0, J_1 2.0)
7-H_A	3.05—2.21	4.80 (d, *J* 6.5)	4.72 (d, *J* 7.5)
7-H_B			
7′-H_A		2.52 (dd, J_1 13.0, J_2 11.0)	2.95 (d, *J* 14.0)
7′-H_B		2.96 (dd, J_1 13.0, $J_2$3.0)	3.05 (d, *J* 14.0)
8-H		2.30 (m)	2.31 (ddd, $J_1 \approx J_2 \approx J \approx$ 6—7)
8′-H		2.69 (m)	
9-H_A	3.93—3.55	3.90—3.77[a]	3.95—3.73 (3 H)[a]
9-H_B			
9′-H_A	5.17 and 4.91 (1 H, 2d, *J* 4.0 and 6.0)	3.67 (dd, J_1 8.5, J_2 6.5)	
9′-H_B		3.96 (dd, J_1 8.5, J_2 6.5)	3.60 (d, *J* 9.0)
O-Me	3.84 (6 H, br s)	3.83 (6 H, s)	3.83 (6 H, s)
O-Me′			
ar-OH	7.34 and 7.33	7.37	7.39
ar-OH′	7.43 and 7.34	7.47	7.48
8′-OH	3.71 and 3.30		3.63
9-OH			3.90
9′-OH	5.53 and 5.19 (1 H, 2d, *J* 4.0 and 6.0)		

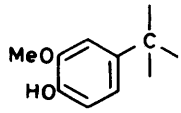
Coupling constants (*J*) in Hz, in $(CD_3)_2CO$.

[a] Different signals superimposed.

matic region extended from δ 6.68—6.90 (6 H). It showed two singlets at δ 6.68 (1 H) and 6.86 (1 H), two double doublets at δ 6.68 (1 H) and 6.81 (1 H) and two doublets at δ 6.86 (1 H) and 6.90 (1 H). The presence of the substituted tetrahydrofuran moiety (**A**) was proposed from the proton spin-decoupling studies.



(A)



(B)

The ^{13}C n.m.r. spectrum (Table 2) was particularly helpful in deducing the carbon skeleton of compound (**1**). The assignments were made on the basis of chemical shift calculations and by comparing the values with similar known tetrahydrofuran lignans.[11,12] The noise-decoupled and single frequency off-resonance spectra showed the presence of two methoxy methyl carbons (2q, δ 57.47), three methylene carbons (t, δ 34.01, 61.03, and 73.71), three methine carbons (d, δ 43.52, 53.93, and 83.70), and twelve aromatic carbons, out of which six are quaternary (s, δ 133.47, 136.67, 145.74, 146.53, 148.20 and 148.32) and the remaining six are unsubstituted aromatic carbon atoms (d, δ 110.38, 113.11, 114.86, 116.28, 119.32, and 121.89).

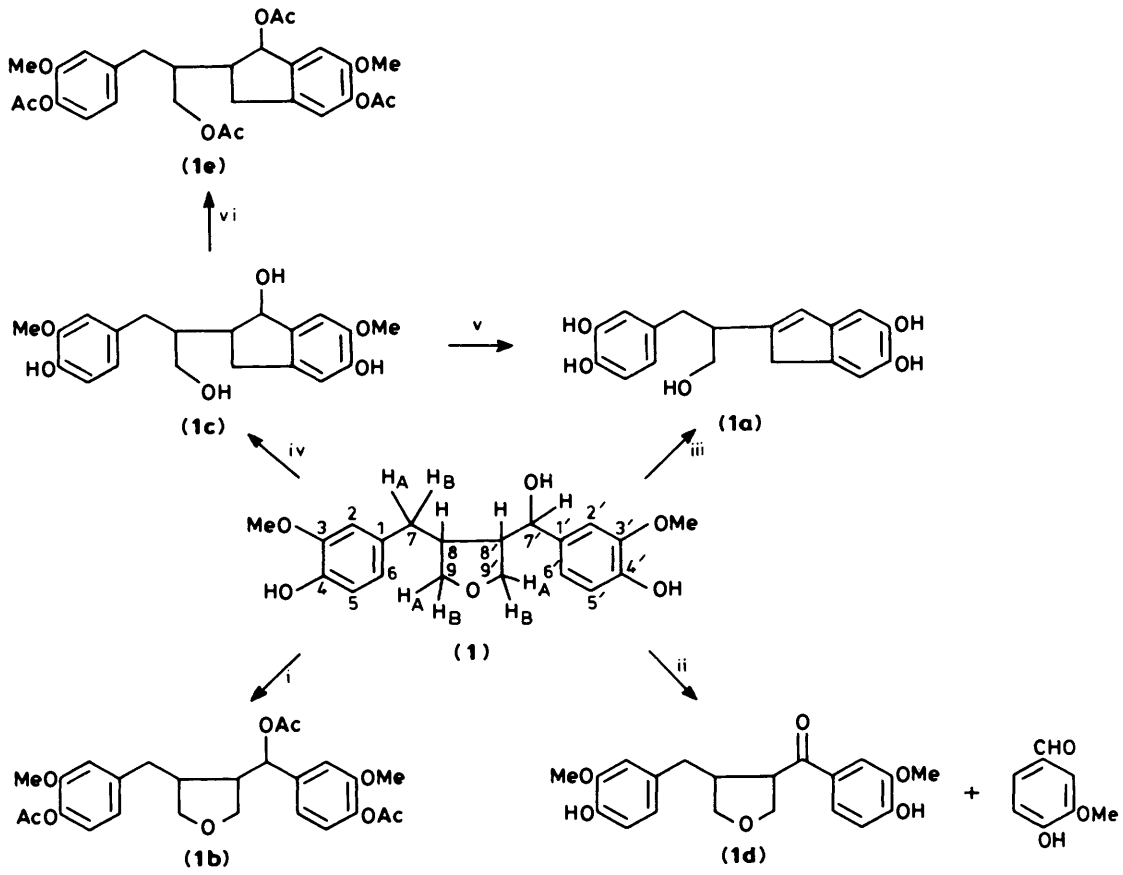
Further evidence for structure (**1**) was obtained from a study of its chemical reactions (Scheme 1).

Acetylation by acetic anhydride in pyridine of (**1**) yielded a tri-acetate (**1b**), the elemental and mass spectral analysis (M^+, 486) of which supported the molecular formula $C_{26}H_{30}O_9$. Its i.r. spectrum showed bands at 1 745 and 1 765 cm^{-1} for the carbonyl groups of the acetates. The ^1H n.m.r. spectrum of (**1b**) showed one singlet at δ 2.30 (6 H) for two phenolic acetoxy groups and one singlet at δ 2.04 (3 H) for one alcoholic acetoxy group.[13]

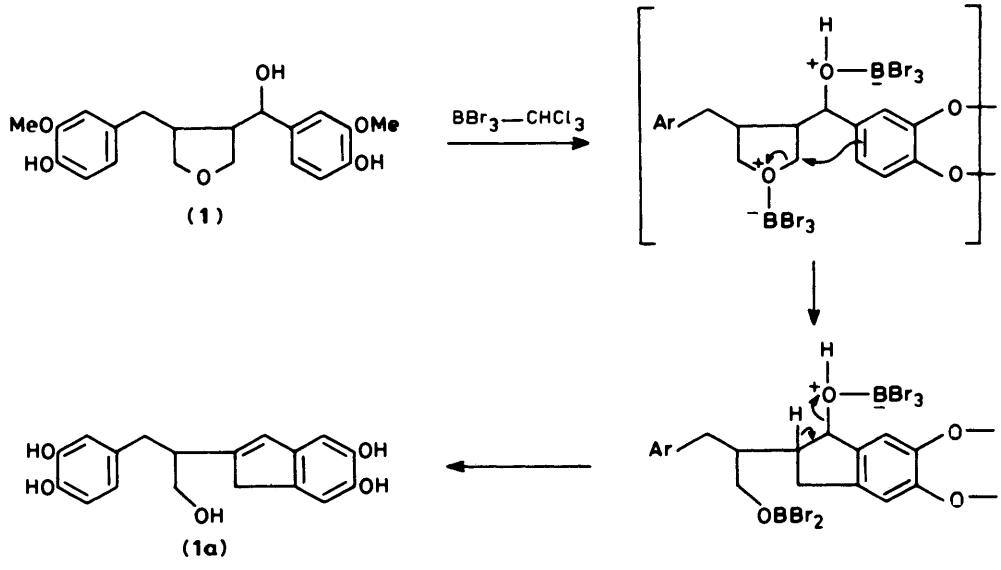
Jones oxidation of (**1**) gave vanillin and a ketone (**1d**); the former was identified by its mixed m.p. and superimposable i.r. spectrum and its isolation from the oxidation products of (**1**) confirmed the presence of the tri-substituted aromatic nucleus (**B**) (above). The mass spectrum (M^+, 358) of (**1d**) showed the loss of two mass units from (**1**) and its i.r. spectrum showed bands at 3 520 and 3 200 cm^{-1} for hydroxy groups and 1 680 cm^{-1} for a conjugated ketone, indicating that the hydroxy group is secondary in nature.

Demethylation of (**1**) by BBr_3 in $CHCl_3$ gave (**1a**). Elemental and mass spectral analysis (M^+, 314) supported the molecular formula $C_{18}H_{18}O_5$ for (**1a**). Its i.r. spectrum showed a broad band at 3 200 cm^{-1} for hydroxy groups and no band in the region for ethers. The ^1H n.m.r. spectrum of (**1**) showed six protons in the aromatic region, whereas there were only five aromatic protons and one singlet at δ 6.24 in (**1a**). There were no signals for methoxy groups. This could be explained by suggesting an internal rearrangement such as the opening of the tetrahydrofuran ring followed by cyclisation and dehydration to give an indene derivative (Scheme 2).

Acid hydrolysis of (**1**) yielded (**1c**), whose molecular formula was found to be $C_{20}H_{24}O_6$ by elemental and mass spectral analysis (M^+, 360). Its i.r. spectrum showed a broad band at 3 300 cm^{-1} and no band in the region for ethers. Acetylation of (**1c**) yielded the tetra-acetate (**1e**), confirming the presence of four hydroxy groups in (**1c**). The tetra-acetate (m.p. 152—153 °C, $C_{28}H_{32}O_{10}$) suggested that the benzylic hydroxy group (C-7) was intact in (**1c**) after the hydrolysis. However, this hydroxy group was lost when (**1c**) was treated with BBr_3 in $CHCl_3$ to give (**1a**). This could be due to the facile formation of an indan derivative (cyclised product) by internal rearrangement. The ^1H n.m.r. spectrum of (**1c**) integrated for only five protons in the aromatic region which supported the formation of an indan nucleus.



Scheme 1. *Reagents: i.* Ac_2O–Py, 24 h, room temp.; ii, Jones reagent, 0—5 °C, 4 h; iii, BBr_3–$CHCl_3$, stir, 5 h, room temp.; iv, 5% HCl, reflux, 10—12 h; v, BBr_3–$CHCl_3$, stir, 1 h, room temp; vi, Ac_2O–Py, 24 h, room temp.



Scheme 2.

The mass spectrum of (**1**) gave peaks at *m/z* 360 (M^+), 330 (M^+ − 2Me), 180, 137 (100%), 151, 123, and 93 which are due to the fragments (**a**), (**b**), (**c**), (**d**), and (**e**) (see Figure) in accord with similar lignans.[14]

Experimental

M.p.s were determined on a Lab. Hosp melting point apparatus and are uncorrected. U.v. spectra were taken in methanol on a Perkin-Elmer spectrophotometer and i.r. spectra were recorded

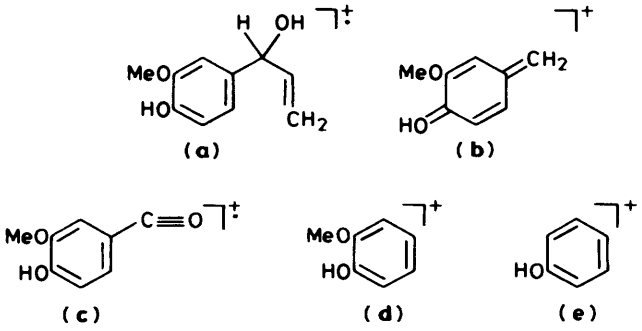


Figure.

either as Nujol mulls or in chloroform on a Perkin-Elmer Grating spectrophotometer. Optical rotations were measured with a Bellingham and Stanley (no. 470507) Polarimeter. ^{1}H N.m.r. spectra were obtained by using Varian XL-100 and Bruker 250 and 500 MHz spectrometers with $CDCl_3$ and $(CD_3)_2CO$ as solvents and $SiMe_4$ as the internal standard. Mass spectral studies were carried out on a Varian MAT 112S spectrometer. Light petroleum refers to the fraction b.p. 40—60 °C.

Isolation of the Phenolic Lignan (**1**).—Dried stems of *Tinospora cordifolia* Miers were finely powdered (5 kg) and extracted with chloroform (20 l) in a Soxhlet apparatus. The extract was concentrated under reduced pressure and the resultant mass was subjected to a preliminary chromatographic separation on silica gel (ratio 1:30) with 0—70% ethyl acetate in light petroleum as eluant. The fraction obtained by elution with 40% ethyl acetate in light petroleum containing phenolic lignan as the major component (0.25 g) was purified by multiple (× 3) preparative t.l.c. It was further purified by repeated crystallisations from 50% ethyl acetate–light petroleum to give (**1**) as white flakes (0.25 g), m.p. 168 °C, $[\alpha]_D^{22}$ −30.0° (*c* 0.50, Me_2CO) (Found: C, 66.15; H, 6.5. $C_{20}H_{24}O_6$ requires C, 66.6; H, 6.6%); $\lambda_{max.}$(MeOH) 205.0, 232.5, and 285.0 nm (ε 16 000 and 11 000); $\nu_{max.}$(Nujol) 3 500, 3 470, 3 370, 3 010, 2 920, 1 615, 1 520, 1 470, 1 370, 1 210, 1 180, 980, and 940 cm^{-1}; for ^{1}H n.m.r. data, see Table 1; *m/z* 360 (M^+, 41%), 345 (22), 330 (17), 180 (38), 151 (72), 137 (100), 124 (53), 93 (35), 77 (40), and 65 (50).

Acetylation of Compound (**1**).—A solution of the lignan (**1**) (20 mg, 0.05 mmol) in acetic anhydride (0.5 ml) in pyridine (0.5 ml) was kept at room temperature for 24 h and then refluxed at 70 °C for 2 h. The reaction mixture was then poured over crushed ice, neutralised with 5% HCl, and extracted with $CHCl_3$. The solution was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to dryness. Chromatography on silica gel with ethyl acetate–light petroleum (40:60) as eluant yielded (**1b**) (15 mg), m.p. 119—120 °C, $[\alpha]_D^{22}$ +36.3° (*c* 1.1, $CHCl_3$) (Found: C, 64.25; H, 6.25. $C_{26}H_{30}O_9$ requires C, 64.19; H, 6.17%); $\lambda_{max.}$(MeOH) 223.0, 274.3, and 278.3 nm (ε 15 000 and 10 000); $\nu_{max.}$($CHCl_3$) 1 765, 1 745, 1 615, 1 310, 1 475, 1 370, 1 270, 1 035, 960, 910, and 875 cm^{-1}; for ^{1}H n.m.r. data see Table 1; *m/z* 486 (M^+, 20%), 444 (5), 402 (5), 384 (10), 367 (12), 342 (15), 205 (50), 151 (80), 137 (100), 91 (20), 77 (22), and 65 (15).

Oxidation of Compound (**1**).—A solution of the lignan (**1**) (20 mg, 50 mmol) in acetone (5 ml) was oxidised with Jones reagent (50 mmol) at 0—5 °C for 4 h. The solution was then poured into cold water and extracted with chloroform, and the extract was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to dryness. Chromatography on silica gel with chloroform as eluant yielded vanillin (3 mg, mixed m.p. 80 °C, and superimposable i.r. spectrum) and with chloroform–methanol (95:5) as eluant yielded (**1d**) (4 mg), m.p. 118—120 °C; $[\alpha]_D^{22}$ −18.1° (*c* 0.55 $CHCl_3$) (Found: C, 66.8; H, 6.0. $C_{20}H_{22}O_6$ requires C, 67.03; H, 6.11%); $\lambda_{max.}$(MeOH) 229.0, 287.0, and 311.0 (ε 10 500 and 9 500); $\nu_{max.}$($CHCl_3$) 3 520, 3 500—3 200, 1 680, 1 610, 1 510, 1 370, 1 120, 1 020, 1 040, and 850 cm^{-1}; for ^{1}H n.m.r. data see Table 1; *m/z* 385 (M^+, 30%), 343 (20), 328 (9), 191 (60), 175 (35), 151 (80), 137 (100), 123 (40), 95 (35), and 77 (20).

Demethylation of Compound (**1**).—A solution of compound (**1**) (15 mg, 41 mmol) in dry chloroform (3 ml) was cooled to 0 °C and BBr_3 (0.5 ml) was added dropwise with constant stirring. The reaction mixture was allowed to attain room temperature after which it was stirred for a further 5 h. The mixture was then evaporated to dryness on a water-bath and the residue co-evaporated with methanol (3 × 8 ml). The reddish residue obtained was dried *in vacuo*. Column chromatography on silica gel with chloroform–methanol (95:5) as eluant yielded (**1a**) (7 mg), m.p. 102—105 °C, $[\alpha]_D^{22}$ +10.0° (*c* 0.65, Me_2CO) (Found: C, 68.5; H, 5.55. $C_{18}H_{18}O_5$ requires C, 68.79; H, 5.73%); $\lambda_{max.}$(MeOH) 208.5 and 287.5 nm (ε 15 500 and 10 200); $\nu_{max.}$(Nujol) 3 500—3 200br, 1 615, 1 520, 1 380, 1 280, 1 080, 1 010, and 880 cm^{-1}; for ^{1}H n.m.r. data see Table 1; *m/z* 314 (M^+, 40%), 297 (9), 273 (12), 161 (20), 118 (35), 105 (100), 91 (85), and 77 (80).

Acid Hydrolysis of Compound (**1**).—A solution of the lignan (**1**) (20 mg, 50 mmol) in acetone (5 ml) was refluxed with 5% HCl (50 mmol) on a water bath for 10—12 h. The solution was then poured over crushed ice and extracted with $CHCl_3$. The extract was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to dryness. Chromatography on silica gel with ethyl acetate–light petroleum (75:25) as eluant yielded (**1c**) (12 mg), m.p. 148—150 °C, $[\alpha]_D^{22}$ +34.2° (*c* 0.70, Me_2CO) (Found: C, 66.1; H, 6.5. $C_{20}H_{24}O_6$ requires C, 66.6; H, 6.6%); $\lambda_{max.}$(MeOH) 211.0, 230.0, and 284.0 nm (ε 15 000 and 11 000); $\nu_{max.}$(Nujol) 3 540, 3 500, 3 300, 1 610, 1 590, 1 380, 1 280, 1 170, 1 060, and 900 cm^{-1}; for ^{1}H n.m.r. data see Table 1; *m/z* 360 (M^+, 100%), 342 (9), 312 (70), 284 (20), 175 (80), 153 (25), 137 (85), 91 (30), 77 (25), and 65 (15).

Acetylation of Compound (**1c**).—A solution of the acid-hydrolysed product (**1c**) (20 mg, 0.05 mmol) in acetic anhydride (0.5 ml) in pyridine (0.5 ml) was kept at room temperature for 24 h after which it was refluxed at 70 °C for 1 h. The reaction mixture was poured over crushed ice, neutralised with 5% HCl, and extracted with $CHCl_3$. The extract was washed with aqueous sodium hydrogen carbonate and water, dried and evaporated to dryness. Chromatography of the residue on silica gel with ethyl acetate–light petroleum (1:1) as eluant yielded the tetra-acetate (**1e**) (14 mg), m.p. 152—153 °C, $[\alpha]_D^{22}$ +66.6 (*c* 0.50, $CHCl_3$) (Found: C, 63.3; H, 5.85. $C_{28}H_{32}O_{10}$ requires C, 63.6; H, 6.06%); $\lambda_{max.}$(MeOH) 204.0, 217.0, 232.0, and 280.0 nm (ε 12 000 and 9 500); $\nu_{max.}$($CHCl_3$) 1 765, 1 745, 1 610, 1 520, 1 470, 1 430, 1 370, 1 220, 1 130, 1 040, and 920 cm^{-1}; for ^{1}H n.m.r. data see Table 1; *m/z* 528 (M^+, 5%), 486 (7), 468 (20), 426 (49), 409 (30), 384 (25), 366 (35), 324 (45), 308 (15), 294 (10), 224 (60), 206 (55), 151 (100), 123 (40), 93 (30), and 77 (27).

Demethylation of Compound (**1c**).—A solution of compound (**1c**) (15 mg, 41 mmol) in dry chloroform (5 ml) was cooled to 0 °C and BBr_3 (0.5 ml) was added dropwise with constant stirring. The reaction mixture was allowed to attain room temperature and the stirring was continued for a further hour.

The solvent was then evaporated to dryness on a water-bath and the residue co-evaporated with methanol (3 × 5 ml). The reddish residue was dried *in vacuo* and then subjected to column chromatography on silica gel with chloroform–methanol (95:5) as eluant to yield (**1a**) (8 mg), m.p. 102—104 °C.

Acknowledgements

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