Stilbene Glycosides from *Guibourtia coleosperma*: Determination of Glycosidic Connectivities by Homonuclear Nuclear Overhauser Effect Difference Spectroscopy

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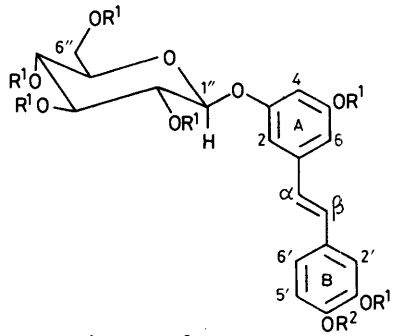
Two novel stilbene glycosides, 3,4'-dimethoxy- and 3,3'-dihydroxy-4'-methoxy-5-[*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyloxy]stilbene, have been obtained from *Guibourtia coleosperma*. Connectivities of glycosidic moieties in these and other mono- and bio-sides have been established by ^{1}H n.m.r. nuclear Overhauser effect difference spectroscopy. Such an approach may prove useful in cases where alternative methods towards achieving the same goal are hampered by limited sample quantitites.

We have recently[1] demonstrated the natural occurrence of a novel class of condensed tannins in the heartwood of Rhodesian copalwood (*Guibourtia coleosperma*). These bi- and tri-flavanoids are based on (*E*)-3,4',5-trihydroxy- and 3,3',4'5-tetrahydroxy-stilbenes and 2,3-*cis*- and 2,3-*trans*-4', 7-dihydroxyflavan-3,4-diols.[2] Since stilbenes are widely claimed[3–6] to possess antifungal properties, we focussed on their presence in the bark, sapwood, and durable[7] heartwood of *G. coleosperma* and now report on the identification of a series of (*E*)-stilbene glycosides.

Despite availability of a wealth of modern organic and spectroscopic strategies, evolution in the chemistry of glycosides is still hampered by two fundamental problems, *i.e.* determination of both the position and mode of linkage, not only of glycosyl to aglycone moiety, but also of connectivity of glycosidic units in oligosaccharides. Existing methodology involves degradative studies, often on limited quantities of material, under conditions where sensitive aglycones do not survive, multi-step syntheses in low overall yields, or spectroscopic methods requiring substantial sample quantities.[8] Availability of the above stilbene glycosides and alternative carbohydrates prompted us to embark on a programme of solving these problems by relatively simple n.m.r. techniques suitable for samples in the order of 10 mg. Such an approach is substantiated by successful elaboration of ^{1}H n.m.r. nuclear Overhauser effect (n.O.e.) difference spectroscopy to related problems in structural elucidation of condensed tannins.[9–11]

Results and Discussion

The bark and sapwood of *G. coleosperma* afforded the known stilbene glucosides rhaponticin[12,13] [(**1**); (*E*)-β-D-glucopyranosyl-3',5-dihydroxy-4'-methoxystilbene] and astringin[13,14] [(**3**); (*E*)-β-D-glucopyranosyl-3',4',5-trihydroxystilbene], which were purified and identified as their *O*-acetyl derivatives (**2**) and (**4**) by means of ^{1}H and ^{13}C n.m.r. spectroscopy (Tables 1 and 2 respectively).† ^{1}H N.m.r. data confirm an *O*-β-D-glucopyranosyl unit [δ 4.86, 4.90; both d, *J* 7.5 Hz, anomeric H for (**2**) and (**4**) respectively] and a 3,3',4',5-tetra-oxygenated (*E*)-stilbene moiety [δ 6.74, 6.90; 6.73, 6.82; both d, *J* 16.5 Hz, vinylic system of (**2**) and (**4**) respectively]. The presence of the β-D-glucopyranosyl unit on ring A is apparent from non-equivalence of 2- and 6-H in both (**2**) and (**4**) (*cf.* ref. 2). N.O.e. difference spectroscopy (Table 3) enabled allocation of the *O*-methyl function in (**2**) to C-4' (B) *via* association of this resonance (δ 3.30, s) to 5'-H (δ 6.54, d, *J* 8.5 Hz). Similar association of the anomeric proton with both 2- and 4-H(A) unambiguously confirms coupling of the glucosyl unit to 3-OMe(A) in both (**2**) and (**4**). Notable also is the prominent association of the anomeric hydrogen to those in the glucosyl moiety (3''- and 5''-H) bearing a 1,3-diaxial relationship. Such observation may usefully be implemented in unravelling of the glycosidic spinning patterns in more complex analogues (see below).



(**1**) R^1 = H, R^2 = Me
(**2**) R^1 = Ac, R^2 = Me
(**3**) R^1 = R^2 = H
(**4**) R^1 = R^2 = Ac

In the sapwood, monosides (**1**) and (**3**) are accompanied by the novel‡ (*E*)-3,4'-dimethoxy-5-[*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyloxy]stilbene (**6**). The ^{1}H n.m.r. spectrum (Table 1) of the *O*-acetyl derivative (**7**) exhibits in the aromatic and olefinic region three double doublets (δ 6.96, 6.85, and 6.69, *J* 2.0 and 2.0 Hz), an AA'BB' system (δ 6.80, 7.34, both d, *J* 9.0 Hz), and an (*E*)-olefinic pattern (δ 6.95, 7.07, both d, *J* 16.5 Hz). When taken in conjunction with the presence of two aromatic methoxyl resonances (δ 3.52, 3.31, both s), the above data indicate a 3,4',5-trioxygenated (*E*)-stilbene moiety substituted at 3-OH(A) with the remaining

† Although both glucosides are known compounds, a short discussion of those ^{1}H n.m.r. data of relevance to the present objectives appears to be appropriate.

‡ The parent 4',5-dihydroxy compound (**5**) has previously been obtained from *Terminalia sericea* and the structure assigned by means of degradation studies (E. Bombardelli, E. M. Martinelli, and G. Mustich, *Fitoterapia*, 1975, **46**, 199).

Table 1. ^{1}H N.m.r. (300 MHz) peaks (p.p.m.) of stilbene glycosides (**2**), (**4**), (**7**), and (**9**) in C_6D_6 at 25 °C. Splitting patterns and *J* values (Hz) are given in parentheses

	H	(2)	(4)	(7)	(9)
Stilbene	α	6.74 (d, 16.5)	6.73 (d, 16.5)	6.95 (d, 16.5)	6.77 (d, 16.5)
	β	6.90 (d, 16.5)	6.82 (d, 16.5)	7.07 (d, 16.5)	6.86 (d, 16.5)
	2	7.08 (dd, 2.0, 2.0)	7.05 (dd, 2.0, 2.0)	6.96 (dd, 2.0, 2.0)	7.04 (d, 2.0)
	4	6.88 (dd, 2.0, 2.0)	6.88 (dd, 2.0, 2.0)	6.69 (dd, 2.0, 2.0)	6.89 (t, 2.0)
	6	7.00 (dd, 2.0, 2.0)	6.97 (dd, 2.0, 2.0)	6.85 (dd, 2.0, 2.0)	7.04 (d, 2.0)
	2′	7.23 (d, 2.0)	7.26 (d, 2.0)	6.80 (d, 9.0)	7.24 (d, 2.0)
	6′	7.07 (dd, 2.0, 8.5)	7.02 (dd, 2.0, 8.5)		7.10 (dd, 2.0, 8.5)
	3′			7.34 (d, 9.0)	
	5′	6.54 (d, 8.5)	7.08 (d, 8.5)		6.57 (d, 8.5)
Glucosyl	1″	4.86 (d, 7.5)	4.90 (d, 7.5)	4.99 (d, 7.5)	4.89 (d, 7.5)
	2″	5.57 (dd, 7.5, 9.5)	5.56 (dd, 7.5, 9.5)	5.59 (dd, 7.5, 9.0)	5.55 (dd, 7.5, 9.0)
	3″	5.43 (dd, 9.5, 9.5)	5.44 (dd, 9.5, 9.5)	5.49 (dd, 9.0, 9.0)	5.46 (dd, 9.0, 9.0)
	4″	5.24 (dd, 9.5, 10.0)	5.25 (dd, 9.5, 10.0)	5.17 (dd, 9.0, 10.0)	5.14 (dd, 9.0, 10.0)
	5″	3.30 (m)	3.35 (m)	3.25 (m)	3.32 (m)
	6″	4.05 (dd, 2.5, 12.5)	4.07 (dd, 2.5, 12.5)	3.45 (dd, 6.0, 12.0)	3.49 (dd, 6.0, 12.0)
		4.18 (dd, 5.5., 12.5)	4.19 (dd, 5.5, 12.5)	3.60 (dd, 3.5, 12.0)	3.62 (dd, 3.5, 12.0)
Rhamnosyl	1‴			4.68 (d, 1.5)	4.73 (d, 1.5)
	2‴			5.61 (dd, 1.5, 3.5)	5.62 (dd, 1.5, 3.5)
	3‴			5.65 (dd, 3.5, 10.0)	5.64 (dd, 3.5, 10.0)
	4‴			5.48 (dd, 10.0, 10.0)	5.47 (dd, 10.0, 10.0)
	5‴			3.96 (dq, 10.0, 6.5)	3.95 (dq, 10.0, 6.5)
	6‴(Me)			1.20 (d, 6.5)	1.20 (d, 6.5)
OMe		3.30 (s)		3.52, 3.31 (each s)	3.31 (s)
OAc		1.96, 1.83, 1.78, 1.74, 1.72, 1.67 (each s)	1.87, 1.86, 1.83, 1.79, 1.75, 1.72, 1.68 (each s)	1.83, 1.76, 1.73, 1.72, 1.65, 1.60 (each s)	2.01, 1.99, 1.83, 1.79, 1.73, 1.72, 1.64, 1.62 (each s)

Table 2. ^{13}C N.m.r. (75.432 MHz) peaks[a] (p.p.m.) of stilbene glycosides (**2**), (**4**), (**7**), and (**9**) in C_6D_6

	C	(2)	(4)	(7)	(9)
Stilbene	α	126.46	128.61	126.61	126.52
	β	129.59	129.02	129.72	129.59
	1	140.28	139.78	140.59	140.39
	2	112.91	113.21	108.17	113.11*
	3	158.20	158.14	158.71	158.09†
	4	109.72	110.14	102.68	109.09
	5	152.42	152.40	161.62	152.58†
	6	114.94	115.12	106.85	114.67*
	1′	130.30	135.82	130.23	130.40
	2′	121.28	121.81	128.39	121.41
	3′	140.83	143.09*	114.50	140.83
	4′	151.73	142.48*	160.01	151.69
	5′	112.57	123.89	114.50	112.54
	6′	125.89	124.97	128.39	125.94
Glucosyl	1″	99.17	99.10	98.98	98.85
	2″	71.67	71.68	71.88	71.66
	3″	73.25	73.22	73.30	73.10
	4″	68.71	68.72	69.93	69.91
	5″	72.35	72.38	73.43	73.48
	6″	62.01	62.02	67.08	66.88
Rhamnosyl	1‴			98.43	98.35
	2‴			69.93	69.91
	3‴			69.84	69.91
	4‴			71.28	71.20
	5‴			67.30	67.32
	6‴ (Me)			17.71	17.71
OMe		55.53		55.25, 54.89	55.52
$OCOCH_3$		20.72—20.23 (6 × s)	20.25—20.73 (7 × s)	20.52—20.36 (6 × s)	20.36—20.85 (8 × s)
OCOMe		170.00—168.14 (6 × s)	169.99—167.49 (7 × s)	169.92—168.93 (6 × s)	169.91—168.10 (8 × s)

[a] Allocation effected by ^{1}H–^{13}C heteronuclear correlations. *·† signals may be interchanged within columns.

hydroxy groups being methylated. The ^{1}H n.m.r. data further suggest the presence of an *O*-α-L-rhamnopyranosyl (δ 4.68, d, *J* 1.5 Hz, anomeric H; δ 1.20, d, *J* 6.5 Hz, 5‴-Me) and an *O*-β-D-glucopyranosyl unit (δ 4.99, d, *J* 7.5 Hz, anomeric H; δ 5.17, dd, *J* 9.0 and 10.0 Hz, 4″-H). The remaining glycosidic protons on the *O*-acetyl-bearing carbons, however, resonate in a narrow region (δ 5.70—5.40), which leads to severe signal overlap. These multiplicities were elucidated by extraction of the appropriate columns from a 2D *J*-resolved experiment. Linkage of the rhamnosyloxy unit to C-6″ of the glucosyl moiety is evident

Table 3. Proton associations based on n.O.e. difference spectroscopy for stilbene glycosides (**2**), (**4**), (**7**), and (**9**) in C_6D_6

		% N.O.e.			
From	To	(**2**)	(**4**)	(**7**)	(**9**)
1″-H(G)*	2-H(A)	2.44	2.44	4.84	1.22‡
	4-H(A)	3.79	5.03	6.50	3.89
	3″-H(G)	2.91	3.01	4.21	4.01
	5″-H(G)	5.45	4.11	5.22	3.51
1‴-H(R)*	6″-H(G)			2.32	2.21
3-OMe(A)	4-H(A)			6.5	
	6-H(A)			6.6	
4′-OMe(B)	5′-H(B)	3.51		†	3.12
5‴-H(R)	3‴-H(R)			3.71	2.68

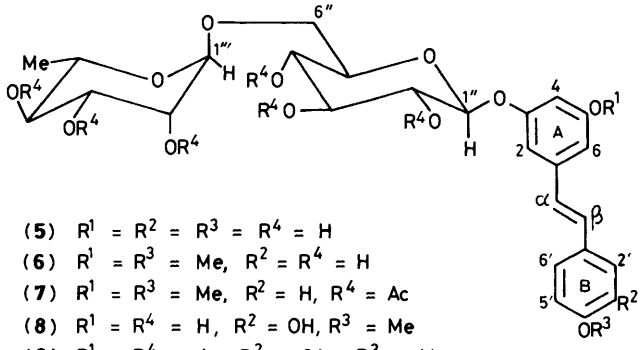
* G = glucosyl, R = rhamnosyl. † N.O.e. irrelevant for placing of OMe. ‡ Approximation due to signal overlap.

Table 4. Proton associations based on n.O.e. difference spectroscopy for acteoside (**10**), isoacteoside (**11**), and bioside (**12**) in $CDCl_3$

		% N.O.e.		
From	To	(**10**)	(**11**)	(**12**)
1-H(G)*	α-H	3.99†	6.45†	4.70
	3-H(G)	0.90	3.42	3.99
	5-H(G)	3.99†	6.45†	2.96
1′-H(R)*	3-H(G)	3.57	6.63	21.38
	α-H (caffeoyl)	0.23		
	β-H (caffeoyl)	0.27		
3-H(G)	1′-H(R)	‡	8.20	9.53
	1-H(G)	‡	2.26	3.13

* G = glucosyl, R = rhamnosyl. † Approximation due to signal overlap. ‡ Omitted due to overlap with OMe resonances.

from n.O.e. association (Table 3) between the anomeric proton of the former and one of the non-equivalent C-6″ methylene protons (δ 3.45, dd, *J* 6.0 and 12.0 Hz), thus unequivocally establishing the presence of a rutinosyl moiety.* Its coupling to the stilbene unit *via* 3-OH(A) follows from association of the glucosyl anomeric proton with two of the double doublets (δ 6.96, 2-H; δ 6.69, 4-H). This mode of coupling also explains non-equivalence of 2- and 6-H(A) as was also observed for monosides (**2**) and (**4**). Once again, the n.O.e. association between the anomeric proton of the glucosyl unit and the axial 3- and 5-H assisted in allocation of proton resonances.

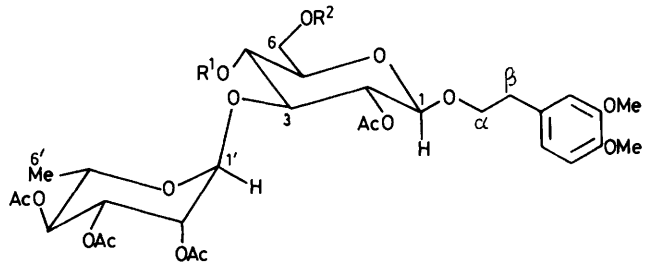


(**5**) $R^1 = R^2 = R^3 = R^4 = H$
(**6**) $R^1 = R^3 = Me$, $R^2 = R^4 = H$
(**7**) $R^1 = R^3 = Me$, $R^2 = H$, $R^4 = Ac$
(**8**) $R^1 = R^4 = H$, $R^2 = OH$, $R^3 = Me$
(**9**) $R^1 = R^4 = Ac$, $R^2 = OAc$, $R^3 = Me$

The heartwood affords, in addition to the condensed tannins based on stilbenes (ref. 2) and monoside (**1**), the first tetra-oxygenated stilbene bioside, (*E*)-3,3′-dihydroxy-4′-methoxy-5-[*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyloxy]-stilbene (**8**), which was purified and identified as the octa-*O*-acetyl derivative (**9**). Its ^1H n.m.r. spectral data (Table 1) reveals a close structural resemblance to that of the trioxygenated stilbene bioside (**7**) except for replacement of the AA′BB′ system in (**7**) with an ABC pattern in (**9**). Allocation of the *O*-methyl function (δ 3.31, s) to C-4′(B) follows from n.O.e. association (Table 3) of these protons and the 5′-H(B) doublet (δ 6.57, *J* 8.5 Hz). The association of the anomeric hydrogen (δ 4.73, d, *J* 1.5 Hz) of the *O*-α-L-rhamnopyranosyl unit (δ 1.20, d, *J* 6.5 Hz, 5‴-Me) with the C-6″ methylene proton (δ 3.49, dd, *J* 6.0 and 12.0 Hz) of the *O*-β-D-glucopyranosyl moiety (δ 4.89, d, *J* 7.5 Hz, anomeric H) similarly defines C-6″–O–C-1‴ connectivity of the sugar units. Linkage of the rutinosyl residue to 3-OH(A) of the stilbene is again confirmed by n.O.e. association of the glucosyl anomeric proton to both 2- (δ 7.04, d, *J* 2.0 Hz) and 4-H(A) (δ 6.89, t, *J* 2.0 Hz), as well as the non-equivalence of the latter two protons.

The ^{13}C n.m.r. spectral data (Table 2) of biosides (**7**) and (**9**) reflect their close structural resemblance. Chemical-shift values of the anomeric carbons confirm the mode of linkage of both rhamnosyl to glucosyl and of the latter to the stilbene moiety.

In order to establish more general applicability, the aforementioned approach was extended to alternative glycosides. The biosides acteoside (**10**), isoacteoside (**11**), and (**12**),[15] with



(**10**) R^1 = (*E*)-3,4-dimethoxycinnamoyl, R^2 = Ac
(**11**) R^1 = Ac, R^2 = (*E*)-3,4-dimethoxycinnamoyl
(**12**) $R^1 = R^2$ = Ac

3–1′ connectivity of *O*-β-D-gluco- and *O*-α-L-rhamno-pyranosyl moieties all exhibit the expected n.O.e. associations (Table 4). Notable is the prominent effect between the anomeric hydrogens of the rhamnosyl units and 3-H of the glucosyls, thus unambiguously confirming the position of linkage of the sugar moieties.† The presence of the β-(3,4-dimethoxyphenyl)ethyl residue at C-1 of the glucosyl unit is evident from strong association between the hydrogen at this carbon and one of the non-equivalent α-hydrogens. Furthermore, the association of the rhamnosyl anomeric hydrogen with the vinylic protons of the C-4 (*E*)-3,4-dihydroxycinnamoyl moiety in acteoside (**10**) and absence thereof in isoacteoside (**11**) provides strong evidence of substitution of such a unit to respectively C-4 and C-6 in biosides (**10**) and (**11**).†

* Establishment of 3–1′ connectivity of sugar moieties in glycopeptides has recently[8] been achieved by two-dimensional heteronuclear correlation *via* long-range coupling (COLOC), such approach, however, requiring substantial sample quantities.

† For bioside (**12**) establishment of 3–1′ connectivity involved an eleven-step synthesis in low overall yield (ref. 15).

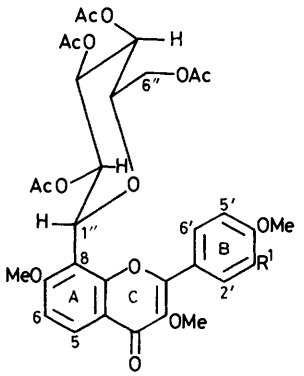
‡ Such distinction has previously been established by means of circular dichroic data (R. Cooper, P. H. Solomon, I. Kubo, K. Nakanishi, J. N. Shoolery, and J. L. Occolowitz, *J. Am. Chem. Soc.*, 1980, **102**, 7955).

Table 5. Proton associations based on n.O.e. difference spectroscopy for C–C-linked glucosides (**13**),* (**14**),* and (**15**)†

From	To	% N.O.e. (**13**)	% N.O.e. (**14**)	% N.O.e. (**15**)
7-OMe(A)	6-H(A)	3.19	2.57	
	1″-H(G)	0.61	1.79	
2″-H(G)	2′-H(B)	0.72	1.06	
	6′-H(B)	0.72	1.08	
4″-H(G)	2′-H(B)	1.12	1.04	
	6′-H(B)	1.12	1.06	
2′-OMe(A)	1″-H(G)			5.98
4′-OMe(A)	2″-H(G)			2.27
	5′-H			11.36
1″-H(G)	2′-OMe(A)			1.97
	3″-H(G)			6.25
	5″-H(G)			1.11

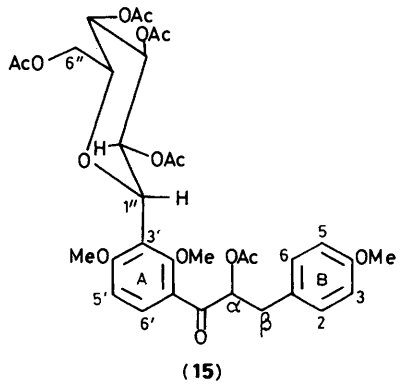
* In $(CD_3)_2SO$. † In $CDCl_3$.

Attention was finally focussed on the carbon–carbon-linked flavonol glucosides 3,4′,7-trimethoxy-8-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)- (**13**) and 3,3′,4′,7-tetramethoxy-8-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-flavone (**14**), and the methyl ether acetate (**15**) of the dihydro-α-hydroxychalcone coatline A.[16] As may be judged from Table 5, less convincing n.O.e. correlations were obtained, e.g. the weak association between 7-OMe(A) and the anomeric proton in both (**13**) and (**14**). This observation may partly be due to severe restrictions



(**13**) R^1 = H

(**14**) R^1 = OMe



(**15**)

* N.O.e. difference spectroscopy has previously been utilized elegantly in conformational analysis of oligosaccharides (H. Thøgersen, R. U. Lemieux, K. Bock, and B. Meyer, *Can. J. Chem.*, 1982, **60**, 44).

on rotation about the C–C bond (*cf.* ref. 16), thus 'fixing' the glucosyl unit in a preferred conformation relative to this bond. Such an assumption is supported by association of both 2″- and 4″H-glucosyl) with 2′- and 6′-H(B) and absence of n.O.e. effects between 1″-and 3″-H (glucosyl) and the aforementioned B-ring protons. Steric compression involving 2″-OAc (glucosyl) and 7-OMe(A) thus presumably forces the latter into a position not favourable for association with 1″-H (glucosyl). In the methyl ether acetate (**15**) (9 mg sample) of coatline A, prominent n.O.e. associations are evident between 2′-OMe and the anomeric hydrogen, and from 4′-OMe to 2″-H (glucosyl). Owing to restrictions imposed on rotation about the C-3′–C-1″ bond by interaction of the 2-OAc (glucosyl) and methoxy substituents of ring A, the n.O.e. associations presumably also reflect a preferred conformation of the glucosyl moiety relative to this bond.

The above approach whereby both connectivity of glycosidic moieties and the position of linkage of sugar units to aglycones may be assigned by n.O.e. difference spectroscopy is, to the best of our knowledge, novel* and may usefully complement existing methods of solving these problems, especially in cases where limited quantities of material are available. In view of the claimed antifungal properties of stilbenes, their presence may well contribute towards high durability of the heartwood of *G. coleosperma*.

Experimental

^1H and ^{13}C N.m.r. spectra were recorded on a Bruker AM-300 spectrometer for C_6D_6, $CDCl_3$, and $(CD_3)_2SO$ solutions with Me_4Si as internal standard. The n.O.e. difference spectra were recorded by methods outlined in the literature.[17–19] T.l.c. was performed on precoated Merck plastic sheets (silica gel 60 PF_{254}, 0.25 mm) and the plates were sprayed with H_2SO_4–HCHO (40:1 v/v) after development. Preparative plates (p.l.c.), 20 × 20 cm, Kieselgel PF_{254} (1.0 mm) were air-dried and used without prior activation. Separations on Sephadex LH-20 columns (5 × 100 cm) were in ethanol. Fractions (25 ml each) were collected on a rotary fraction collector, starting with introduction of the sample on the column. Acetylations were performed in acetic anhydride–pyridine at ambient temperatures. Evaporations were done under reduced pressure at *ca.* 50 °C in a rotary evaporator.

Isolation and Identification of Stilbene Glycosides

Finely powdered bark (2 kg) of *Guibourtia coleosperma* was extracted with methanol (4 × 2 l) and the combined extracts were treated with hexane to remove fats and waxes. The methanol was removed under reduced pressure to give a brown powder (140 g), a portion (15 g) of which was subjected to chromatography on Sephadex LH-20. The contents of plates 25—100 (800 mg) was separated by means of p.l.c. in benzene–acetone–methanol (11:6:3 v/v) to give a main band at R_F 0.45 (580 mg). Acetylation followed by p.l.c. in benzene–acetone (9:v/v) afforded (*E*)-3,3′ di acetoxy-4′-methoxy-5-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)stilbene [(**2**), 380 mg, R_F 0.35] as a light yellow oil. ^1H and ^{13}C N.m.r. spectral data are in Tables 1 and 2 respectively.

Drillings (4 kg) of the sapwood were similarly extracted with methanol and the combined extracts were treated with hexane. Evaporation of the solvent gave a light-brown powder (90 g), a sample (20 g) of which was subjected to chromatography on Sephadex LH-20. Fractions were combined as follows: 1 (plates (134—146; 253 mg), 2 (plates 186—248; 460 mg), 3 (plates 249—305; 246 mg). Fraction 3 was purified by means of p.l.c. in benzene–acetone–methanol (6:3:1 v/v) to give a single band at R_F 0.19 (176 mg). Acetylation afforded (*E*)-3,3′,4′-triacetoxy-

5-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)stilbene (**4**) as a light yellow oil (180 mg). ^{1}H and ^{13}C n.m.r. spectral data are in Tables 1 and 2 respectively.

Fraction 2 was purified by means of p.l.c. [benzene–acetone–methanol (6:3:1 v/v)] to give a main band at R_F 0.15 (350 mg). Successive acetylation and p.l.c. separation in benzene–acetone (9:1 v/v) afforded the stilbene glucoside (**2**) (275 mg, R_F 0.33), identical with that obtained from the bark.

Fraction 1 was separated by means of p.l.c. in benzene–acetone–methanol (6:3:1 v/v) to give a main band at R_F 0.2 (189 mg). This was acetylated and the mixture was subjected to p.l.c. in 1,2-dichloroethane–acetone (19:1 v/v) to give (*E*)-3,4′-*dimethoxy*-5-[2,3,4-*tri*-O-*acetyl*-6-O-(2,3,4-*tri*-O-*acetyl*-α-L-*rhamnopyranosyl*)-β-D-*glucopyranosyloxy*]*stilbene* (**7**) (160 mg, R_F 0.40) as a white amorphous powder (Found: C, 58.9. H, 6.0. $C_{40}H_{48}O_{18}$ requires C, 58.8; H, 5.9%); ^{1}H and ^{13}C n.m.r. data are in Tables 1 and 2 respectively.

Heartwood drillings (3 kg) were extracted with moist ethyl acetate (4 × 2 l), and the solvent was evaporated off to give a dark brown powder (100 g). A portion (20 g) of this was chromatographed on Sephadex LH-20. The contents of plates 153—191 (400 mg) was further purified by p.l.c. in benzene–acetone–methanol (11:6:3 v/v) to give two bands at R_F 0.41 (55 mg) and 0.17 (106 mg). Following acetylation and p.l.c. separation [benzene–acetone (9:1 v/v)], fraction 2 afforded the stilbene glucoside (**2**) (80 mg, R_F 0.33). Similar treatment of fraction 1 gave (E)-3,3′-*diacetoxy*-4′-*methoxy*-5-[2,3,4-*tri*-O-*acetyl*-6-O-(2,3,4-*tri*-O-*acetyl*-α-L-*rhamnopyranosyl*)-β-D-*glucopyranosyloxy*]*stilbene* (**9**) (40 mg, R_F 0.36) as a white amorphous powder (Found: C, 57.3; H, 5.6. $C_{43}H_{50}O_{21}$ requires C, 57.2; H, 5.6%); ^{1}H and ^{13}C n.m.r. data are in Tables 1 and 2 respectively.

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