

## ISOFLAVANOID CONSTITUENTS FROM *DALBERGIA MONETARIA*

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Key Word Index—*Dalbergia monetaria*; Leguminosae—Papilionoideae; rotenoids; 12-dihydrorotenone.

**Abstract**—The structures and isolation of eight compounds from *Dalbergia monetaria* seeds are described. Four of them are known rotenoids. In addition to a new isoflavone and its 7- $\beta$ -D-glucoside, the first 12-dihydrorotenone, 12-dihydrodalbinol, and its 8'- $\beta$ -D-glucoside were identified.

### INTRODUCTION

*Dalbergia monetaria* L. is a plant of wide distribution in French Guyana. Extraction of the defatted seeds of this previously unworked species with methanol led, after extensive chromatography, to the isolation of eight compounds, four of which are new natural products. The separation and purification procedure for these isolates are presented in detail in the Experimental. The compounds are described herein according to their polarity and are tentatively named compounds A-H.

### RESULTS AND DISCUSSION

Compound A (1), mp 184-186°,  $[\alpha]_D^{25}$  -114° (c 0.9; chloroform); UV  $\lambda_{max}$  236 ( $\epsilon$  18 000), 244 ( $\epsilon$  15 400) and 292 nm ( $\epsilon$  19 000). The EI mass spectrum of 1 showed the molecular ion at  $m/z$  410 corresponding to  $C_{23}H_{22}O_7$  and a base peak at  $m/z$  192  $[C_{11}H_{12}O_3]^+$ , probably due to the fragment ion  $\left[ \begin{array}{c} \text{MeO} \\ | \\ \text{MeO} \end{array} \begin{array}{c} \text{O} \\ | \\ \text{O} \end{array} \right]^+$ . These spectral data suggested that compound A was identical with the known rotenoid amorphigenin (1) [1]. The identification was confirmed by  $^1H$ NMR data as shown in Table 1. Amorphigenin occurs in several genera of the Leguminosae ([1] and references therein) but, to date, it has not been found in the *Dalbergia*.

Compound B (2) analysed for  $C_{23}H_{22}O_8$  ( $[M]^+$ ,  $m/z$  at 426) and proved to be dalbinol (2) [2] by comparison of their UV and  $^1H$ NMR data (Table 1). The identification was substantiated by the following. Acetylation of 2 afforded a monoacetate (3) and a diacetate (4). Treatment of 2 with dilute hydrochloric acid gave a crystalline compound, mp 204-210°, which was identified (UV, MS,  $^1H$ NMR) with the known 6a,12a-dehydroamorphigenin (5). On acetylation, the latter gave a crystalline monoacetate (6) of 8'-O-acetyl-6a,12a-dehydroamorphigenin [2,3].

Compound C (7), an amorphous solid,  $[\alpha]_D^{25}$  -136.8° (c 0.5; methanol),  $C_{23}H_{24}O_8$ . Its EI mass spectrum registered a signal at  $m/z$  410 corresponding to the loss of 1 mol of water from the molecular ion. Neither the CI- nor the FAB-mass spectrum displayed a signal corresponding to the molecular ion but only a peak at  $m/z$  411. In contrast to the rotenones 1 and 2, the UV spectrum of compound C

had only a benzenoid chromophore ( $\lambda_{max}$  287 nm,  $\epsilon$  4000), suggesting the lack of a carbonyl function at C-12. Furthermore, the  $^1H$ NMR spectrum showed a significant upfield shift of H-11 ( $\delta$ 6.94, see Table 1).

These observations indicated that compound C was 12-dihydrodalbinol (7). On acetylation it afforded a mixture of di- and tri-acetates.

Dalbinol (2) was treated with sodium borohydride to give a triol (8) (see Experimental) which proved to be different from compound C (7). However, periodic acid oxidation of both triols 7 and 8 led to the same crystalline product (9):  $C_{23}H_{22}O_8$  (MS:  $[M]^+$  at  $m/z$  426); UV  $\lambda_{max}$  238 ( $\epsilon$  20 700) and 282 ( $\epsilon$  19 000) nm. The  $^1H$ NMR data given in Table 1 fully support structure 9 and show, in particular, a downfield signal at  $\delta$ 10.52 assignable to the -CHO group. Furthermore, acetylation of 9 afforded the monoacetate 10,  $C_{25}H_{24}O_9$  ( $[M]^+$  at  $m/z$  468) ( $^1H$ NMR data in Table 1).

It is assumed, as reported for amorphigenin 7 [1], that the reduction of the 12-oxo group of dalbinol by sodium borohydride gives an  $\alpha$ -hydroxyl group and that the triol 8 would have a *trans*-glycol group. The natural product, compound 7, must possess a *cis*-glycol group and is therefore (12*S*)-dihydrodalbinol. In agreement with this conclusion, compound 7 readily gives a crystalline acetonide, mp 108-111°,  $C_{26}H_{28}O_8$  ( $[M]^+$  at  $m/z$  468) whereas the triol 8 failed to form this derivative.

Compound C (7), a 12-dihydrorotenoid, has not previously been isolated from nature.

The mass spectrum of compound D (11) indicated the molecular formula  $C_{18}H_{16}O_6$  ( $[M]^+$  at  $m/z$  328). The UV spectrum, which showed maxima at 241 ( $\epsilon$  16 700), 248 ( $\epsilon$  16 600) and 297 nm ( $\epsilon$  12 000), is characteristic of an isoflavone skeleton. The  $^1H$ NMR spectrum showed signals for three methoxyl groups and a characteristic singlet at  $\delta$ 8.15 due to the proton at C-2. These physical properties correspond to those reported for a synthetic isoflavone [4] which had been shown to be a precursor of amorphigenin (1) in *Amorpha fruticosa* L. seedlings and was detected in this source, in trace amounts by an isotopic dilution technique [5].

\* Compounds E-H proved to be  $\beta$ -glucosides since they underwent smooth enzymatic hydrolysis to give the aglycones 1, 2, 7 and 11, respectively, and D-glucose (identified by TLC in two solvent systems). Compound E

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N° : 26.820 ex 1

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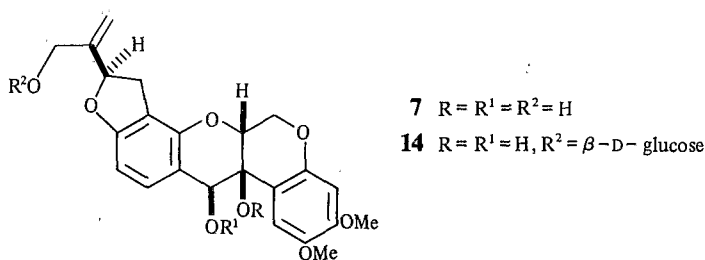
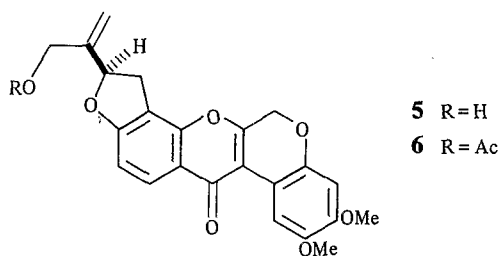
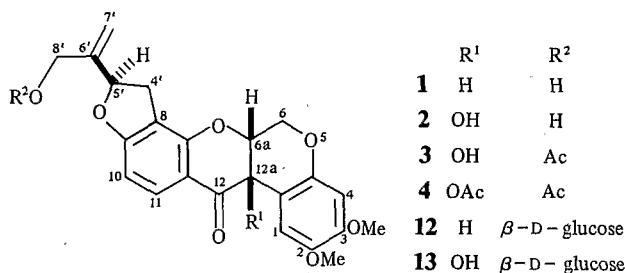
Table 1. <sup>1</sup>H NMR spectral data of the aglycones and their derivatives

Compound	H-1	H-4	H-6	H-6a	H-10	H-11	H-12α(β)	H-4'	H-5'	H-7'	H-8'	OMe	OH/OAc
1	6.79 <i>s</i>	6.47 <i>s</i>	4.20 <i>dd</i> (12, 1) 4.63 <i>dd</i> (12, 3)	4.95 <i>m</i>	6.5 <i>d</i> (9)	7.87 <i>d</i> (9)	—	3.06 <i>dd</i> (15, 9) 3.46 <i>dd</i> (15, 9)	5.43 <i>t</i> (9)	5.28 <i>s (br)</i>	4.28 <i>s (br)</i>	3.79 3.83	1.86 <i>s (br)</i> 8'-OH
2	6.59 <i>s</i>	6.49 <i>s</i>	4.48 <i>d</i> (10) 4.66 <i>d</i> (10)	4.58 <i>s (br)</i>	6.51 <i>d</i> (8)	7.82 <i>d</i> (8)	—	3.01 <i>dd</i> (15, 9) 3.40 <i>dd</i> (15, 9)	5.39 <i>t</i> (9)	5.25	4.24	3.73 3.82	2.20 <i>s (br)</i> 8'-OH
3	6.57 <i>s</i>	6.5 <i>s</i>	4.57 <i>s (br)</i>	4.57 <i>s (br)</i>	6.53 <i>d</i> (9)	6.85 <i>d</i> (9)	—	3.01 <i>dd</i> (15, 9) 3.4 <i>dd</i> (15, 9)	5.5 <i>m</i>	5.2 <i>s (br)</i>	4.68 <i>s (br)</i>	3.72 3.82	2.04 <i>s</i> 8'-OAc
4	6.88 <i>s</i>	6.48 <i>s</i>	4.29 <i>d</i> (12, 1) 4.58 <i>d</i> (12, 3)		6.54 <i>d</i> (8)	7.86 <i>d</i> (8)	—	3.01 <i>dd</i> (15, 9) 2.40 <i>dd</i> (15, 9)	5.33 <i>t</i> (9)	5.30 <i>s (br)</i> 5.45 <i>s (br)</i>	4.68 <i>s (br)</i>	3.78 3.83	2.04 <i>s</i> 8'-OAc 2.15 <i>s</i> 12a-OAc
5*	8.9 <i>s</i>	6.78 <i>s</i>	5.08 <i>s</i>		7.0 <i>d</i> (9)	8.33 <i>d</i> (9)	—	3.52 <i>m</i> ( <i>d (br)</i> , 9)	5.8 <i>t</i> (9)	5.47 <i>s (br)</i> 5.60 <i>s (br)</i>	4.60 <i>s (br)</i>	3.78 3.90	—
6	8.33 <i>s</i>	6.45 <i>s</i>	4.92 <i>s</i>		6.81	8.02	—	3.32— 3.80 <i>m</i>	5.45 <i>t</i> (9)	5.3 <i>s (br)</i> 5.45 <i>s (br)</i>	4.69 <i>s (br)</i>	3.82 3.92	2.06 8'-OAc
7	6.71 <i>s</i>	6.34 <i>s</i>	4.45 <i>s (br)</i>	4.32 <i>s (br)</i>	6.24 <i>d</i> (9)	6.94 <i>d</i> (9)	4.98 <i>s</i>	2.90 <i>dd</i> (15, 9) 3.30 <i>dd</i> (15, 9)	5.19 <i>t</i> (9)	5.17	4.10 <i>s (br)</i>	3.75	—

Diacetate	6.71 s	6.31	4.46 s (br)	4.46 s (br)	6.23 d (8)	6.98 d (8)	6.37 s	2.92 dd (15, 8)	5.19 dd (8, 9)	5.18 s (br) 5.23 s (br)	4.6 s (br)	3.74	2.03 OAc 2.12 OAc		
Triacetate	7.04 s	6.27 s	4.63 s (br)	4.63 s (br)	6.23 d (10)	7.10 d (10)	6.31 s		5.20 t (9)	5.2 s (br) 5.3 s (br)	4.56 s (br)	3.72 3.75	1.98 } OAc 2.02 } 2.06 }		
Acetonide	6.84 s	6.43 s	4.48 s (br)	4.20 s (br)	6.45 d (9)	7.18 d (9)	5.3 m	3.0 dd (16, 9)	5.3 m	5.3 m	4.24 s (br)	3.84		1.53 s } Me 1.70 s }	
8-diacetate	7.0 s	6.32 s	4.46 s (br)	4.6 s (br)	6.42 d (9)	7.05 d (9)	(6.09 s)	3.02 dd (15, 9)	5.36 (9)	5.23 s (br) 5.33 s (br)	4.67 s (br)	3.82	1.76 2.03	12-OAc 8'-OAc	
9*	7.42	6.67			6.78 d (9)	7.92 d (9)	—	3.5- 3.9 m	5.53 t (8)		4.62 s (br)	3.67 3.77		10.52 12-CHO	
10	7.21	6.47	4.72 s (br)		6.67 d (8)	7.67 d (8)		3.2- 3.8 m	5.42 t (9)	5.28 s (br) 5.33 s (br)	4.67 s (br)	3.87 3.94	2.02	8'-OAc 12-CHO	

\*Pyridine- $d_5$  as solvent.

Coupling constants ( $J$  in Hz) are given in parentheses.



(12), (mp 186–187°) had the molecular formula  $C_{29}H_{32}O_{12}$  ( $[M]^+$  at  $m/z$  572) with a base peak at  $m/z$  192. On acetylation, compound 12 formed a tetraacetate. On acid and enzyme hydrolysis, 12 gave amorphenigenin (1) and D-glucose and is therefore amorphenigenin-8'- $\beta$ -D-glucoside. This glucoside has been reported (mp 164°) to occur in the seeds of ten species of *Amorpha* [6].

Compound F (13), amorphous solid,  $C_{29}H_{32}O_{13}$  ( $[M]^+$  at  $m/z$  588) proved to be the known dalbin. On acetylation, it gave a pentaacetate and on enzymatic hydrolysis it yielded dalbinol (2) and D-glucose.

Compound G (14), an amorphous solid,  $C_{29}H_{34}O_{13}$ . Its mass spectrum showed, as in the case of 7, a peak at  $m/z$  572 corresponding to  $[M-18]^+$ . Only a benzenoid chromophore ( $\lambda$  287 nm) was evident in its UV spectrum. Acetylation of 14 gave a crystalline pentaacetate, mp 175–180°,  $C_{39}H_{44}O_{18}$ . It showed a  $[M-60]^+$  ion peak and no molecular ion peak in either the EI-, CI- (isobutane), CI-( $NH_3$ ) or FAB mass spectra.

Enzymatic hydrolysis afforded (12*S*)-dihydrodalbinol (7) and D-glucose. Mild periodic acid oxidation (short reaction time) of 14 afforded a crystalline compound 15, mp 139–141°, in which only the  $C_{12-12a}$  *cis*-glycol was cleaved; this was supported by the formation of a tetraacetate,  $C_{37}H_{40}O_{17}$ , the mass spectrum of which had a  $[M]^+$  ion peak at  $m/z$  756. Thus compound G is 12-dihydrodalbin (14) and is a new natural glucoside.

Compound H (16), needles, mp 166–167°,  $C_{24}H_{26}O_{11}$

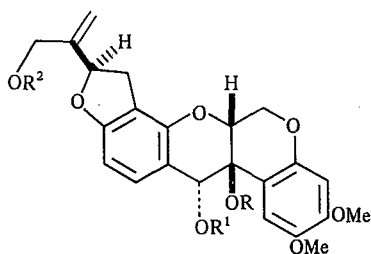
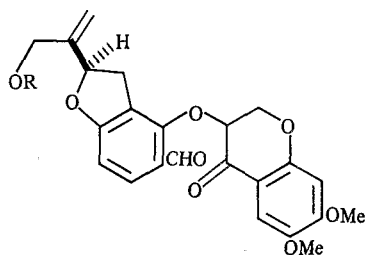
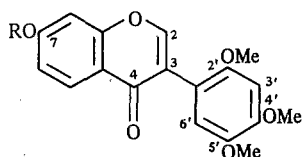
( $[M]^+$  at  $m/z$  490) is the  $\beta$ -D-glucoside of the isoflavone 11 as, on acetylation, it gave a crystalline tetraacetate and on enzymatic hydrolysis it afforded the aglycone 11 and D-glucose. This glucoside has not previously been found in nature.

The larvicidal activity of rotenone and of the natural products 1, 2, 11, 12 and 14 was tested on the 4th instar larvae of *Aedes aegypti* L. (strain Bangui) at a concentration of 10 ppm. 100% mortality was noted for rotenone within 3 days, whereas amorphenigenin 8'- $\beta$ -D-glucoside (12) led to an 85% loss and without the formation of pupae. The other compounds tested showed no significant larvicidal activity.

#### EXPERIMENTAL

Mps were determined on a Büchi apparatus and Kofler hot-stage microscope and are uncorr. Optical rotations were determined at room temp. on a Perkin-Elmer 141 polarimeter. 60 MHz  $^1H$  NMR spectra were taken in  $CDCl_3$ , unless otherwise stated, at 25° using TMS as internal standard. EIMS were taken on an MS 50-AEI spectrometer and CIMS were recorded on a modified [7] MS-9 spectrometer.

*Extraction of D. monettaria seeds.* The ripe seeds (159 g) were powdered and extracted (Soxhlet), first with *n*-hexane and then with MeOH. Evapn of the MeOH gave a residue (59.0 g), which was chromatographed on a silica gel column using  $CHCl_3$ -MeOH (20:1  $\rightarrow$  3:1) as eluant and monitored by TLC to

**8** R = R¹ = R² = H**9** R = H; **10** R = Ac**15** R =  $\beta$ -D-glucose**11** R = H**16** R =  $\beta$ -D-glucose

give fractions (I–VII) (1.2, 1.0, 9.5, 4.6, 2.6, 11.0 and 22.5 g, respectively).

**Chromatography of fraction I** on silica gel ( $C_6H_6$ – $Me_2CO$ , 15:1  $\rightarrow$  6:1) afforded four compounds A (1), B (2), C (7) and D (11) in 0.36, 0.15, 0.096 and 0.007% yield, respectively.

Compound A (1) crystallized as needles ( $C_6H_6$ – $Me_2CO$  or  $C_6H_6$ – $CHCl_3$ ). It was readily identified as amorphenin (1).

Compound B (2) was obtained as an amorphous solid on rechromatography on silica gel ( $C_6H_6$ – $Me_2CO$ ; 8:1);  $[\alpha]_D^{20}$   $-159.4^\circ$  ( $c$  0.5; MeOH). (Found: C, 64.5; H, 5.2. Calc. for  $C_{23}H_{22}O_8$ : C, 64.78; H, 5.2%). UV  $\lambda_{max}^{MeOH}$  nm ( $\epsilon$ ): 236 (8000), 244 sh (14400), 292 (19000). Compound B (2) (50 mg) was dissolved in  $Ac_2O$ – $C_5H_5N$  (10:1) and left at room temp. for 12 hr. Usual work-up followed by purification on prep. TLC ( $C_6H_6$ – $Me_2CO$ , 5:1) gave a monoacetate (8 mg) and a diacetate (35 mg) as shown by  $^1H$ NMR (Table 1).

Compound B (2) (50 mg), when heated with dilute HCl at  $50^\circ$  for 2 hr, then diluted and extracted with  $CHCl_3$ , afforded 6a,12a-dehydroamorphenin (5), which crystallized (MeOH) as yellow needles, mp  $204$ – $210^\circ$  (dec.). UV  $\lambda_{max}^{MeOH}$  nm ( $\epsilon$ ): 236 (30900), 279 (24500), 308 (19000); MS  $m/z$ : 408  $[M]^+$ ;  $^1H$ NMR: see Table 1. Acetylation ( $Ac_2O$ – $C_5H_5N$ , 10:1) gave 8'-O-acetyl-6a,12a-dehydroamorphenin (6), mp  $172$ – $178^\circ$  (dec.) [2, 3].

Reduction of dalbinol (2) (100 mg) in MeOH (8 ml) was carried out with  $NaBH_4$  (30 mg) for 0.5 hr at room temp. Dilution, then removal of the MeOH and extraction with EtOAc gave a residue, on evapn, which was purified by prep. TLC ( $C_6H_6$ – $Me_2CO$ , 2:1). The reduction product (8) crystallized as prisms (MeOH) of 12 $\alpha$ -dihydrodalbinol, mp  $120$ – $125^\circ$ . (Found: C, 64.37; H, 5.5.  $C_{23}H_{24}O_8$  requires: C, 64.48; H, 5.6%).  $[\alpha]_D^{20}$   $-178.2^\circ$  ( $c$  0.5; MeOH); MS  $m/z$ : 428  $[M]^+$  ( $C_{23}H_{24}O_8$ ). The O-diacetate (54 mg) prepared from 2 (60 mg) with  $Ac_2O$ – $C_5H_5N$  was purified

by prep. TLC ( $C_6H_6$ – $Me_2CO$ , 4:1).  $^1H$ NMR: see Table 1.

Compound C (7) was purified by rechromatography on silica gel ( $C_6H_6$ – $Me_2CO$ , 7:1  $\rightarrow$  5:1) and gave an amorphous solid. (Found: C, 64.56; H, 5.6.  $C_{23}H_{24}O_8$  (as above).) Acetylation of 7 (100 mg) afforded after CC (silica gel) ( $C_6H_6$ – $Me_2CO$ , 10:1) a diacetate (50 mg) and a triacetate (15 mg) as shown by  $^1H$ NMR (Table 1).

**Periodic acid oxidation.** Compound C (7) (50 mg) in MeOH (5 ml) was treated with  $HIO_4 \cdot 2H_2O$  (20 mg in 1 ml  $H_2O$ ) for 12 hr at room temp. The product 9 crystallized (MeOH) as prisms (40 mg), mp  $210$ – $212^\circ$ . (Found: C, 64.41; H, 5.42.  $C_{23}H_{22}O_8$  requires: C, 64.79; H, 5.2%). Acetylation ( $Ac_2O$ – $C_5H_5N$ , 10:1) afforded a monoacetate (10), which crystallized as needles (EtOAc–MeOH), mp  $183$ – $180^\circ$ . (Found: C, 63.9; H, 5.2.  $C_{25}H_{24}O_9$  requires: C, 64.2; H, 5.2%).  $[\alpha]_D^{20}$   $+90.6^\circ$  ( $c$  0.32;  $CHCl_3$ );  $^1H$ NMR: see Table 1.

The triol 8 (20 mg) and  $HIO_4 \cdot 2H_2O$  (10 mg in 0.5 ml  $H_2O$ ) was kept at room temp. for 4 hr. Work-up gave a product identical to 9 in all respects (mmp, UV,  $^1H$ NMR, MS).

**Acetonide of compound C (7).** Compound 7 (40 mg) was dissolved in  $Me_2CO$ –HCl (5 ml) (30 ml  $Me_2CO$ –1 drop HCl) and kept for 3 days at room temp. Dilution with  $H_2O$ , removal of the  $Me_2CO$ , and extraction with EtOAc afforded a residue, which was purified by prep. TLC ( $C_6H_6$ – $Me_2CO$ , 4:1). The acetonide (21 mg) crystallized as needles (MeOH), mp  $108$ – $111^\circ$ . (Found: C, 66.5; H, 6.0.  $C_{26}H_{28}O_8$  requires: C, 66.66; H, 6.02%).  $^1H$ NMR: see Table 1; MS  $m/z$ : 468  $[M]^+$ , 453  $[M-Me]^+$ , 410  $[M-Me_2CO]^+$ .

Compound D (11) crystallized from MeOH as needles, mp  $240$ – $242$ . (Found: C, 65.55; H, 4.85. Calc. for  $C_{18}H_{16}O_6$ : C, 65.8; H, 4.9%). Identical (mp, UV,  $^1H$ NMR, MS) with 7-hydroxy-2',4',5'-trimethoxyisoflavone [4].

**Crystallization of fraction II.** Fraction II (1.0 g) was crystallized from EtOAc–MeOH to give compound E (12) (274 mg). The mother liquor was concd, added to fraction III, and the mixture was chromatographed on silica gel ( $CHCl_3$ –MeOH, 15:1  $\rightarrow$  10:1) to yield a further 3.248 g of 12 as prisms, mp  $186$ – $188^\circ$  (lit. [6] mp  $164^\circ$ ). UV  $\lambda_{max}^{MeOH}$  nm: 237, 243 (sh), 293;  $^1H$ NMR ( $C_5D_5N$ ):  $\delta$  7.18 (s, H-1), 6.69 (s, H-4), 6.54 (d, H-10,  $J$  = 9 Hz), 8.08 (d, H-11,  $J$  = 9 Hz), 3.62 (s), 3.64 (s,  $2 \times OMe$ ). Acetylation ( $Ac_2O$ – $C_5H_5N$ , 10:1) of 12 at room temp. followed by purification on prep. TLC ( $C_6H_6$ – $Me_2CO$ , 10:1) gave a tetraacetate as an amorphous solid.  $^1H$ NMR:  $\delta$  6.73 (s, H-1), 6.41 (s, H-4), 6.47 (d, H-10,  $J$  = 8.5 Hz), 7.8 (d, H-11,  $J$  = 8.5 Hz), 3.76 (s), 3.8 (s,  $2 \times OMe$ ), 2.02 (s,  $3 \times OAc$ ), 2.08 (–OAc).

Hydrolysis of 12 (200 mg) with 3 M HCl in  $H_2O$  for 3 hr gave, on extraction with  $CHCl_3$  and subsequent chromatography on silica gel ( $CHCl_3$ –MeOH, 15:1  $\rightarrow$  4:1), a fraction, 'a' (65 mg), which crystallized as needles ( $n$ -hexane–EtOAc), mp  $178$ – $182^\circ$ , identical (mp, UV,  $^1H$ NMR, MS) with amorphenin and fraction 'b' (50 mg) unchanged 12.

The aq. layer, which was neutralized with Amberlite IR-45, contained glucose ( $R_f$  0.38, standard: D-glucose,  $R_f$  0.38).

Fractions IV (4.6 g), V (2.6 g) and VI (11.0 g) were chromatographed on silica gel (Fig. 1).

Compound F (13) was identical (mmp, UV, IR, MS,  $^1H$ NMR) with dalbin. Acetylation of 13 with  $Ac_2O$ – $C_5H_5N$  (10:1) afforded a pentaacetate, which was crystallized from  $H_2O$ –MeOH, mp  $152$ – $156^\circ$  (lit. [8] mp  $141$ – $142^\circ$ ).  $^1H$ NMR:  $\delta$  2.02 (s,  $3 \times OAc$ ), 2.07 (s, OAc), 2.16 (s, OAc).

Compound G (14), amorphous solid. (Found: C, 59.0; H, 5.6.  $C_{29}H_{34}O_{13}$  requires: C, 58.97; H, 5.8%). UV  $\lambda_{max}^{MeOH}$  nm: 287; MS  $m/z$ : 572  $[M-H_2O]^+$ , 412, 410, 381, 208 ( $C_{11}H_{12}O_4$ ) (base peak);  $^1H$ NMR ( $C_5D_5N$ ):  $\delta$  3.54 (s), 3.63 (s,  $2 \times OMe$ ), 5.73 (d, H-12 $\alpha$ ,  $J$  = 1.0 Hz), 6.43 (d, H-10,  $J$  = 8 Hz), 6.62 (s, H-1), 7.35 (dd, H-11,  $J$  = 8 Hz) 7.38 (s, H-1).

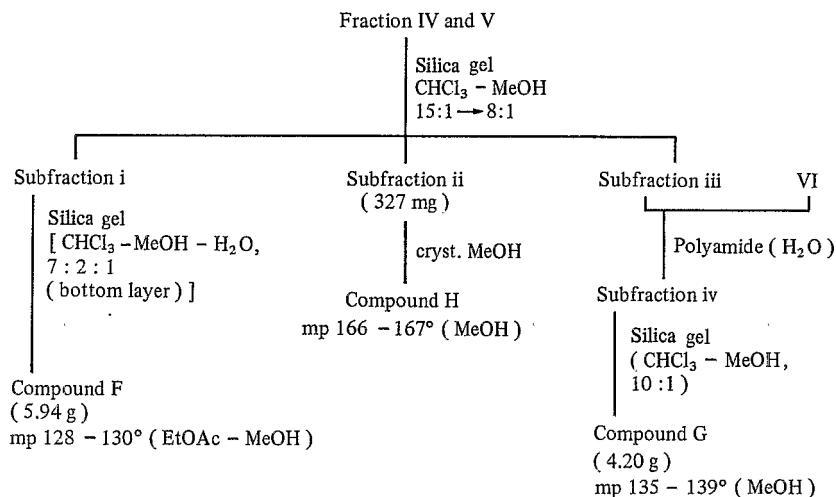


Fig. 1. Separation of fractions IV, V and VI.

Acetylation ( $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ , 10:1) afforded a pentaacetate as needles, mp 175–180° ( $\text{CHCl}_3-\text{MeOH}$ ). (Found: C, 58.25; H, 5.3.  $\text{C}_{39}\text{H}_{44}\text{O}_{18}$  requires: C, 58.5; H, 5.5%). MS  $m/z$ : 740  $[\text{M}-60]^+$ ;  $^1\text{H NMR}$ :  $\delta$  2.02 (s, 3  $\times$  OAc), 2.08 (s, 2  $\times$  OAc), 3.80 (s, 2  $\times$  OMe), 6.30 (d, H-11,  $J = 9$  Hz), 6.37 (s, H-4 and H-12 $\alpha$ ), 6.74 (s, H-1), 6.97 (d, H-10,  $J = 9$  Hz).

Oxidation of **14** (100 mg) in MeOH (5 ml) with  $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$  (40 mg) in  $\text{H}_2\text{O}$  (2 ml) for 2 hr at room temp. yielded a ppt. of **15** which crystallized from MeOH as prisms, mp 139–141°. (Found: C, 59.3; H, 5.2.  $\text{C}_{29}\text{H}_{32}\text{O}_{13}$  requires: C, 59.18; H, 5.5%). MS  $m/z$ : 588  $[\text{M}]^+$ ; Acetylation ( $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ , 10:1) of **15** gave a tetraacetate as prisms (MeOH), mp 104–106°. (Found: C, 59.0; H, 5.2.  $\text{C}_{37}\text{H}_{40}\text{O}_{17}$  requires: C, 58.73; H, 5.3%). MS  $m/z$ : 756  $[\text{M}]^+$ , 331.  $^1\text{H NMR}$ :  $\delta$  3.01 (s, 2  $\times$  OAc), 2.04 (s), 2.08 (s, 2  $\times$  OAc), 3.86 (s), 3.94 (s, 2  $\times$  OMe), 6.47 (s, H-4), 6.65 (d, H-10,  $J = 9$  Hz), 7.2 (s, H-1), 7.67 (d, H-11,  $J = 9$  Hz), 10.0 (s, -CHO).

Compound H (**16**), mp 166–170° (MeOH). (Found: C, 58.5; H, 5.3.  $\text{C}_{24}\text{H}_{26}\text{O}_{11}$  requires: C, 58.78; H, 5.35%). MS  $m/z$ : 490  $[\text{M}]^+$ , 328  $[\text{C}_{18}\text{H}_{16}\text{O}_6]^+$ ;  $^1\text{H NMR}$  ( $\text{C}_5\text{D}_5\text{N}$ ):  $\delta$  3.78 (s), 3.83 (s), 3.86 (s, 3  $\times$  OMe), 6.82 (s, H-3'), 7.2–7.5 (m, H-6, H-6', H-8), 8.14 (s, H-2), 8.36 (d, H-5,  $J = 9$  Hz). Acetylation of **16** ( $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ , 10:1) at room temp. yielded a tetraacetate. EIMS  $m/z$ : 658  $[\text{M}]^+$  ( $\text{C}_{32}\text{H}_{34}\text{O}_{15}$ ).

Hydrolysis of glucosides **12**, **13**, **14** and **16** with  $\beta$ -glucosidase (almond emulsin). Compounds **12**, **13**, **14** and **16** were incubated with  $\beta$ -glucosidase at 37° for 1 day. The reaction mixtures were extracted with EtOAc. The organic extracts were washed, dried and evapd. The residues were purified on columns of silica gel.

The aglycones **1**, **2**, **7** and **11** were obtained (identical mp, TLC and  $^1\text{H NMR}$ ).

The aq. layers were concd and examined by TLC (visualized with aniline hydrogen phthalate).  $R_f$  0.2 ( $n\text{-BuOH}-\text{HOAc}-\text{H}_2\text{O}$ , 4:1:5, upper layer) and 0.38 ( $n\text{-BuOH}-\text{C}_6\text{H}_6-\text{C}_5\text{H}_5\text{N}-\text{H}_2\text{O}$ , 5:1:3:3). Standard: D-glucose.  $R_f$  0.20 and 0.38.

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