Phytochemistry, Vol 24, No 5, pp 1071–1076, 1985
Printed in Great Britain

0031–9422/85 $3 00 + 0 00

ISOFLAVANOID CONSTITUENTS FROM *DALBERGIA MONETARIA*

FUMIKO ABE,* DERVILLA M X DONNELLY,* CHRISTIAN MORETTI† and JUDITH POLONSKY‡

*Department of Chemistry, University College Dublin, Dublin 4, Ireland, †Office de la Recherche Scientifique et Technique Outre-Mer, B P 165, Cayenne, Guyana, ‡Institut de Chimie des Substances Naturelles, CNRS, 91190 Gif-sur-Yvette, France

(*Received* 13 *August* 1984)

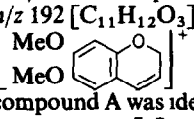
Key Word Index—*Dalbergia monetaria*, Leguminosae–Papilionoideae, rotenoids, 12-dihydrorotenone

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-β-D-glucoside, the first 12-dihydrorotenone, 12-dihydrodalbinol, and its 8′-β-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°, $[\alpha]_D$ −114° (*c* 0 9, chloroform), UV λ_{max} 236 (ε 18 000), 244 (ε 15 400) and 292 nm (ε 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  These spectral data suggested that compound A was identical with the known rotenoid amorphigenin (**1**) [1] The identification was confirmed by ^{1}H 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 ^{1}H 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, ^{1}H 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, $[\alpha]_D^{21}$ −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 (λ_{max} 287 nm, ε 4000), suggesting the lack of a carbonyl function at C-12 Furthermore, the ^{1}H NMR spectrum showed a significant upfield shift of H-11 (δ6 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 λ_{max} 238 (ε 20 700) and 282 (ε 19 000) nm The ^{1}H NMR data given in Table 1 fully support structure **9** and show, in particular, a downfield signal at δ10 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) (^{1}H 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 α-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 (ε 16 700), 248 (ε 16 600) and 297 nm (ε 12 000), is characteristic of an isoflavone skeleton The ^{1}H NMR spectrum showed signals for three methoxyl groups and a characteristic singlet at δ8 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 fructicosa* L seedlings and was detected in this source, in trace amounts by an isotopic dilution technique [5]

Compounds E–H proved to be β-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

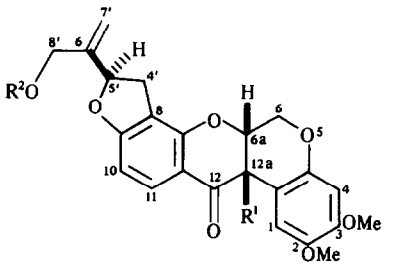
Table 1 ^{1}H NMR spectral data of the aglycones and their derivatives

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 *s*	6 47 *s*	4 20 *dd* (12, 1) 4 63 *dd* (12, 3)	4 95 *m*	6 5 *d* (9)	7 87 *d* (9)	—	3 06 *dd* (15, 9) 3 46 *dd* (15, 9)	5 43 *t* (9)	5 28 *s* (*br*)	4 28 *s* (*br*)	3 79 3 83	1 86 *s* (*br*)	8′-OH
2	6 59 *s*	6 49 *s*	4 48 *d* (10) 4 66 *d* (10)	4 58 *s* (*br*)	6 51 *d* (8)	7 82 *d* (8)	—	3 01 *dd* (15, 9) 3 40 *dd* (15, 9)	5 39 *t* (9)	5 25	4 24	3 73 3 82	2 20 *s* (*br*)	8′-OH
3	6 57 *s*	6 5 *s*	4 57 *s* (*br*)	4 57 *s* (*br*)	6 53 *d* (9)	6 85 *d* (9)	—	3 01 *dd* (15, 9) 3 4 *dd* (15, 9)	5 5 *m*	5 2 *s* (*br*)	4 68 *s* (*br*)	3 72 3 82	2 04 *s*	8′-OAc
4	6 88 *s*	6 48 *s*	4 29 *d* (12, 1) 4 58 *d* (12, 3)		6 54 *d* (8)	7 86 *d* (8)		3 01 *dd* (15, 9) 2 40 *dd* (15, 9)	5 33 *t* (9)	5 30 *s* (*br*) 5 45 *s* (*br*)	4 68 *s* (*br*)	3 78 3 83	2 04 *s* 2 15 *s*	8′-OAc 12a-OAc
5*	8 9 *s*	6 78 *s*	5 08 *s*		7 0 *d* (9)	8 33 *d* (9)	—	3 52 *m* (*d* (*br*), 9)	5 8 *t* (9)	5 47 *s* (*br*) 5 60 *s* (*br*)	4 60 *s* (*br*)	3 78 3 90	—	
6	8 33 *s*	6 45 *s*	4 92 *s*		6 81	8 02	—	3 32–3 80 *m*	5 45 *t* (9)	5 3 *s* (*br*) 5 45 *s* (*br*)	4 69 *s* (*br*)	3 82 3 92	2 06	8′-OAc
7	6 71 *s*	6 34 *s*	4 45 *s* (*br*)	4 32 *s* (*br*)	6 24 *d* (9)	6 94 *d* (9)	4 98 *s*	2 90 *dd* (15, 9) 3 30 dd (15, 9)	5 19 *t* (9)	5 17	4 10 *s* (*br*)	3 75	—	

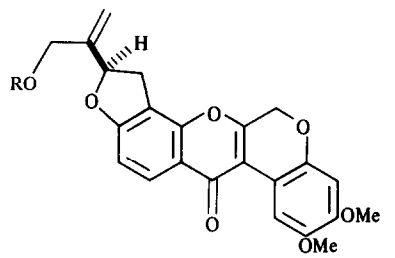
Diacetate	6 71 *s*	6 31	4 46 *s* (*br*)	4 46 *s* (*br*)	6 23 *d* (8)	6 98 *d* (8)	6 37 *s*	2 92 *dd* (15, 8) 3 32 *dd* (15, 9)	5 19 *dd* (8, 9)	5 18 *s* (*br*) 5 23 *s* (*br*)	4 6 *s* (*br*)	3 74	2 03 OAc 2 12 OAc			
Triacetate	7 04 *s*	6 27 *s*	4 63 *s* (*br*)	4 63 *s* (*br*)	6 23 *d* (10)	7 10 *d* (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 2 02 2 06 } OAc			
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) 3 4 *dd* (16, 9)	5 3 *m*	5 3 *m*	4 24 *s* (*br*)	3 84			1 53 *s* 1 70 *s* } Me	
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) 3 42 *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	10 04 12-CHO	

*Pyridine-d_5 as solvent

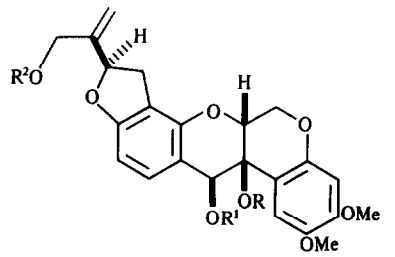
Coupling constants (J in Hz) are given in parentheses



	R^1	R^2
1	H	H
2	OH	H
3	OH	Ac
4	OAc	Ac
12	H	β-D-glucose
13	OH	β-D-glucose



5 R=H
6 R=Ac



7 R = R¹ = R² = H
14 R = R¹ = H, R² = β-D-glucose

(**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 amorphigenin (**1**) and D-glucose and is therefore amorphigenin-8′-β-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 (λ 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

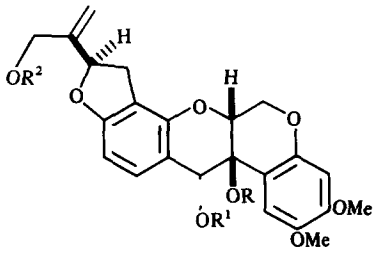
Compound H (**16**), needles, mp 166–167°, $C_{24}H_{26}O_{11}$ ($[M]^+$ at *m/z* 490) is the β-D-glucoside of the isoflavone **11** as, on acetylation, it gave a crystalline tetraacetate and on enzymatic hydrolysis it afforded the aglycone **11** and D-glucose This glucoside has not previously been 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 amorphigenin 8′-β-D-glucoside (**12**) led to an 85% loss and without the formation of pupae The other compounds tested showed no significant larvicidal activity

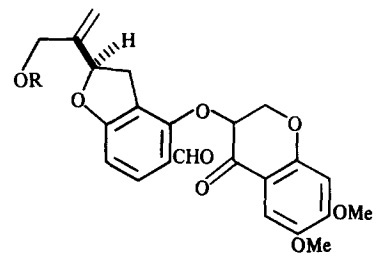
EXPERIMENTAL

Mps were determined on a Buchi apparatus and Kofler hot-stage microscope and are uncorr Optical rotations were determined at room temp on a Perkin–Elmer 141 polarimeter 60 MHz ^{1}H 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 monetaria *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 → 3 1) as eluant and monitored by TLC to

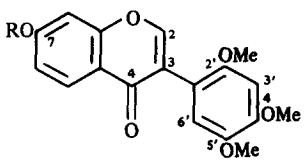


8 R = R¹ = R² = H



9 R = H, **10** R = Ac

15 R = β-D-glucose



11 R = H

16 R = β-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 → 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 amorphigenin (**1**)

Compound B (**2**) was obtained as an amorphous solid on rechromotography on silica gel (C_6H_6–Me_2CO, 8 1), $[\alpha]_D^{20}$ −159 4° (*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 λ_{max}^{MeOH} nm (ε) 236 (8000), 244 sh (14 400), 292 (19 000) 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 ^{1}H NMR (Table 1)

Compound B (**2**) (50 mg), when heated with dilute HCl at 50° for 2 hr, then diluted and extracted with $CHCl_3$, afforded 6a,12a-dehydroamorphigenin (**5**), which crystallized (MeOH) as yellow needles, mp 204–210° (dec) UV λ_{max}^{MeOH} nm (ε) 236 (30 900), 279 (24 500), 308 (19 000), MS *m/z* 408 $[M]^+$, ^{1}H NMR see Table 1 Acetylation (Ac_2O–C_5H_5N, 10 1) gave 8′-*O*-acetyl-6a,12a-dehydroamorphigenin (**6**), mp 172–178° (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 12α-dihydrodalbinol, mp 120–125° (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° (*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) ^{1}H NMR see Table 1

Compound C (**7**) was purified by rechromatography on silica gel (C_6H_6–Me_2CO, 7 1 → 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 ^{1}H NMR (Table 1)

Periodic acid oxidation Compound C (**7**) (50 mg) in MeOH (5 ml) was treated with HIO_4 $2H_2O$ (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° (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° (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° (*c* 0 32, $CHCl_3$), ^{1}H NMR see Table 1

The triol **8** (20 mg) and HIO_4 $2H_2O$ (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, ^{1}H 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° (Found C, 66 5, H, 6 0 $C_{26}H_{28}O_8$ requires C, 66 66, H, 6 02%) ^{1}H 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, ^{1}H 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 → 10 1) to yield a further 3 248 g of **12** as prisms, mp 186–188° (lit [6] mp 164°) UV λ_{max}^{MeOH} nm 237, 243 (sh), 293, ^{1}H NMR (C_5D_5N) δ 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 × 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 ^{1}H NMR δ 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 × OMe), 2 02 (*s*, 3 × 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 → 4 1), a fraction, 'a' (65 mg), which crystallized as needles (*n*-hexane–EtOAc), mp 178–182°, identical (mp, UV, ^{1}H NMR, MS) with amorphigenin 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, ^{1}H 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° (lit [8] mp 141–142°) ^{1}H NMR δ 2 02 (*s*, 3 × 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 λ_{max}^{MeOH} nm 287, MS *m/z* 572 $[M-H_2O]^+$, 412, 410, 381, 208 ($C_{11}H_{12}O_4$) (base peak), ^{1}H NMR (C_5D_5N) δ 3 54 (*s*), 3 63 (*s*, 2 × OMe), 5 73 (*d*, H-12α, *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)

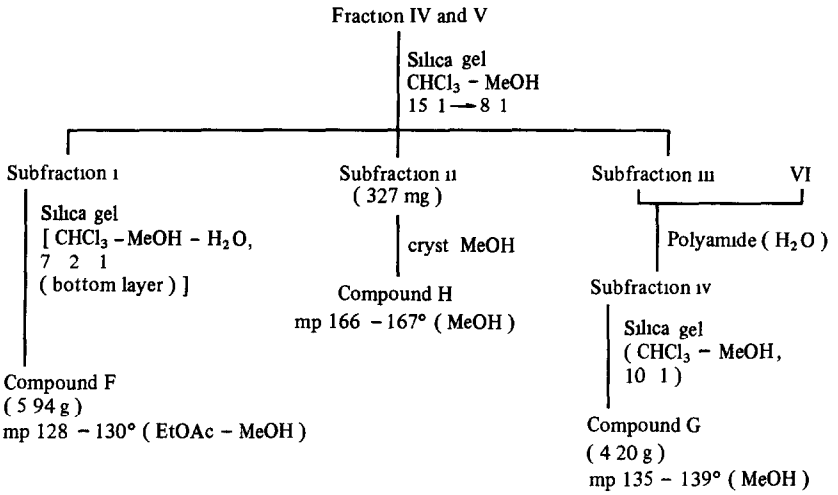


Fig 1 Separation of fractions IV, V and VI

Acetylation (Ac_2O–C_5H_5N, 10 1) afforded a pentaacetate as needles, mp 175–180° ($CHCl_3$–MeOH) (Found C, 58 25, H, 5 3 $C_{39}H_{44}O_{18}$ requires C, 58 5, H, 5 5%) MS *m/z* 740 $[M-60]^+$, ^1H NMR δ2 02 (*s*, 3 × OAc), 2 08 (*s*, 2 × OAc), 3 80 (*s*, 2 × OMe), 6 30 (*d*, H-11, J = 9 Hz), 6 37 (*s*, H-4 and H-12α), 6 74 (*s*, H-1), 6 97 (*d*, H-10, J = 9 Hz)

Oxidation of **14** (100 mg) in MeOH (5 ml) with HIO_4 $2H_2O$ (40 mg) in H_2O (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 $C_{29}H_{32}O_{13}$ requires C, 59 18, H, 5 5%) MS *m/z* 588 $[M]^+$, Acetylation (Ac_2O–C_5H_5N, 10 1) of **15** gave a tetraacetate as prisms (MeOH), mp 104–106° (Found C, 59 0, H, 5 2 $C_{37}H_{40}O_{17}$ requires C, 58 73, H, 5 3%) MS *m/z* 756 $[M]^+$, 331 ^1H NMR δ3 01 (*s*, 2 × OAc), 2 04 (*s*), 2 08 (*s*), 2 × OAc), 3 86 (*s*), 3 94 (*s*, 2 × 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 $C_{24}H_{26}O_{11}$ requires C, 58 78, H, 5 35%) MS *m/z* 490 $[M]^+$, 328 $[C_{18}H_{16}O_6]^+$, ^1H NMR (C_5D_5N) δ3 78 (*s*), 3 83 (*s*), 3 86 (*s*, 3 × 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** (Ac_2O–C_5H_5N, 10 1) at room temp yielded a tetraacetate EIMS *m/z* 658 $[M]^+$ ($C_{32}H_{34}O_{15}$)

Hydrolysis of glucosides **12**, **13**, **14** *and* **16** *with β-glucosidase (almond emulsin)* Compounds **12**, **13**, **14** and **16** were incubated with β-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 ^1H NMR)

The aq layers were concd and examined by TLC (visualized with aniline hydrogen phthalate) R_f 0 2 (*n*-BuOH–HOAc–H_2O, 4 1 5, upper layer) and 0 38 (*n*-BuOH–C_6H_6–C_5H_5N–H_2O, 5 1 3 3) Standard D-glucose R_f 0 20 and 0 38

Acknowledgements—We thank the National Board for Science and Technology for the award of a Fellowship (to F A) We are grateful to Mr Rageau (O R S T O M , Boudy) for the larvicidal tests

REFERENCES

1 Crombie, L (1984) *Nat Prod Rep* **1**, 3
2 Chibber, S S and Khera, U (1978) *Phytochemistry* **17**, 1442
3 Claisse, J , Crombie, L and Peace, R (1964) *J Chem Soc* 6023
4 Fukui, K , Nakayama, M , Hatanaka, M , Okamoto, T and Kawase, Y (1963) *Bull Chem Soc Jpn* 397
5 Crombie, L , Dewick, P M and Whiting, D A (1973) *J Chem Soc Perkin Trans* 1, 1285
6 Kasymou, A U , Kondratenko, E S and Abubakirov, N K (1968) *Khim Prir Soedin* **4**, 326, (1969) *Chem Abstr* **70** 88190r
7 Varenne, P , Bardey, B , Longevialle, P and Das, B C (1977) *Bull Soc Chim Fr* 886
8 Chibber, S S and Khera, U (1979) *Phytochemistry* **18**, 188