ISOFлавANOID 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-β-D-glucoside, the first 12-dihydrorotenone, 12-dihydroladinol, 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°, [x]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 C23H22O7 and a base peak at m/z 192 [C11H12O3] +, probably due to the fragment ion \[\text{MeO} \mid \text{MeO} \]. 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 had only been found in nature.

Compound B (2) analysed for C23H24O8 ([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, \([x]_{D}^{28} = 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 1H NMR spectrum showed a significant upfield shift of H-11 (δ 6.94, see Table 1). These observations indicated that compound C was 12-dihydroladinol (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_{24}O_{8} (MS: [M]+ at m/z 426); UV λ max 238 (ε 20 700) and 282 (ε 19 000) nm. The 1H NMR data given in Table 1 fully support structure 9 and show, in particular, a downfield signal at δ 5.12 assignable to the –CHO group. Furthermore, acetylation of 9 afforded the monoacetate 10, C_{23}H_{24}O_{8} ([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 α-hydroxy 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 (12S)-dihydroladinol. In agreement with this conclusion, compound 7 readily gives a crystalline acetone, mp 108–111°, C_{23}H_{24}O_{8} ([M]+ at m/z 468) whereas the triol 8 failed to form this derivative.

Compound C (7), a 12-dihydrotorenone, 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 1H NMR spectrum showed signals for three methoxyl groups and a characteristic singlet at δ 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 β-glucosides since they underwent smooth enzymatic hydrolysis to give the aglycones 1, 2, 7 and 11, respectively, and α-glucoside (identified by TLC in two solvent systems). Compound E
Table 1. $^1$H NMR spectral data of the aglycones and their derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>H-1</th>
<th>H-4</th>
<th>H-6</th>
<th>H-6a</th>
<th>H-10</th>
<th>H-11</th>
<th>H-12αβ</th>
<th>H-4'</th>
<th>H-5'</th>
<th>H-7'</th>
<th>H-8'</th>
<th>OMe</th>
<th>OH/OAc</th>
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<tbody>
<tr>
<td>1</td>
<td>6.79 s</td>
<td>6.47 s</td>
<td>4.20 dd (12, 1)</td>
<td>4.95 m (9)</td>
<td>6.5 d (9)</td>
<td>7.87 d (9)</td>
<td>—</td>
<td>3.06 dd (15, 9)</td>
<td>5.43 t (9)</td>
<td>5.28 s (br)</td>
<td>4.28 s (br)</td>
<td>3.79</td>
<td>1.86 s (br)</td>
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<tr>
<td>2</td>
<td>6.59 s</td>
<td>6.49 s</td>
<td>4.48 d (10)</td>
<td>4.58 s (br) (8)</td>
<td>6.51 d (8)</td>
<td>7.82 d (8)</td>
<td>—</td>
<td>3.01 dd (15, 9)</td>
<td>5.39 t (9)</td>
<td>5.25</td>
<td>4.24</td>
<td>3.73</td>
<td>3.82</td>
</tr>
<tr>
<td>3</td>
<td>6.57 s</td>
<td>6.5 s</td>
<td>4.57 s (br) (10)</td>
<td>4.57 s (br) (9)</td>
<td>6.53 d (9)</td>
<td>6.85 d (9)</td>
<td>—</td>
<td>3.01 dd (15, 9)</td>
<td>5.5 m</td>
<td>5.2 s (br)</td>
<td>4.68 s (br)</td>
<td>3.72</td>
<td>3.82</td>
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<tr>
<td>4</td>
<td>6.88 s</td>
<td>6.48 s</td>
<td>4.29 d (12, 1)</td>
<td>4.58 d (12, 3)</td>
<td>6.54 d (8)</td>
<td>7.86 d (8)</td>
<td>—</td>
<td>3.01 dd (15, 9)</td>
<td>5.33 t (9)</td>
<td>5.30 s (br)</td>
<td>4.68 s (br)</td>
<td>3.78</td>
<td>2.04 s</td>
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<tr>
<td>5*</td>
<td>8.9 s</td>
<td>6.78 s</td>
<td>5.08 s (12, 3)</td>
<td>7.0 d (9)</td>
<td>8.33 d (9)</td>
<td>—</td>
<td>3.52 m (d br, 9)</td>
<td>5.8 t (9)</td>
<td>5.47 s (br)</td>
<td>4.60 s (br)</td>
<td>3.78</td>
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<tr>
<td>6</td>
<td>8.33 s</td>
<td>6.45 s</td>
<td>4.92 s</td>
<td>6.81</td>
<td>8.02</td>
<td>—</td>
<td>3.32-3.80 m (9)</td>
<td>5.45 t (9)</td>
<td>5.3 s (br)</td>
<td>4.69 s (br)</td>
<td>3.82</td>
<td>2.06</td>
<td>8'-OAc</td>
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<tr>
<td>7</td>
<td>6.71 s</td>
<td>6.34 s</td>
<td>4.45 s (br) (12, 3)</td>
<td>4.32 s (br) (9)</td>
<td>6.24 d (9)</td>
<td>6.94 d (9)</td>
<td>4.98 s</td>
<td>2.90 dd (15, 9)</td>
<td>5.19 t (9)</td>
<td>5.17</td>
<td>4.10 s (br)</td>
<td>3.75</td>
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<td></td>
<td>6.71 s 6.31</td>
<td>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) 4.6 s (br) 3.74 2.63 OAc 2.12 OAc</td>
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<td>Triacetate</td>
<td>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) 4.56 s (br) 3.72 1.98 2.02 OAc 2.06</td>
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<tr>
<td>Acetonide</td>
<td>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) 3.02 dd (15, 9) 5.36 5.27 s (br) 4.67 s (br) 3.82 1.76 1.20 OAc 1.06</td>
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<tr>
<td>8-diacetate</td>
<td>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 5.33 s (br) 4.67 s (br) 3.82 1.76 1.20 OAc 1.06</td>
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<tr>
<td>9*</td>
<td>7.42 6.67 6.78 d (9) 7.92 d (9) 3.5 t 3.9 m (8) 5.53 t 5.36 3.67 4.62 s (br) 4.67 s (br) 3.87 2.02 8'-OAc 10.04 12-CHO</td>
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<td>10</td>
<td>7.21 6.47 4.72 s (br) 6.67 d (8) 7.67 d (8) 3.2 3.8 m (9) 5.28 s (br) 5.33 s (br) 4.67 s (br) 3.87 2.02 8'-OAc 10.04 12-CHO</td>
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*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 amorphigenin (1) and D-glucose and is therefore amorphigenin-8'-ß-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 (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 (12S)-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_{28}H_{26}O_{11} ([M]^+ at m/z 490) is the ß-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'-ß-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 30-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
The reduction product on evapn, which was purified by prep. TLC (C6H6-Me2CO, 2:1) and gave an amorphous solid. (Found: C, 64.56; H, 5.6. C23H22O8 (as above) Acetylation of 7 (100 mg) afforded after CC (silica gel) (C6H6-Me2CO, 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 HIO4.2H2O (20 mg in 1 ml H2O) 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. C22H22O8 requires: C, 64.79; H, 5.2%). Acetylation of (Ac2O-C2H5N, 10:1) afforded a monoacetate (10), which crystallized as needles (EtOAc-MeOH), mp 183-185°. (Found: C, 63.9; H, 5.2. C22H22O8 requires: C, 64.2; H, 5.2%). 

Hydrogenation of compound F (110 mg) was carried out with NaBH4 (30 mg) for 0.5 hr at room temp. Dilution, then Acetylation (Ac2O-C2H5N, 10:1) gave 8'-O-acetyl-6a,12a-dehydroamorphigenin (8), mp 204-210° (dec.). UV A&O4 nm: 236, 292 (19000). Compound F (110 mg) was identical (mp, UV, 'H NMR, MS) with amorphigenin and compound G (110 mg) was 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 liquid was concd, added to fraction III, and the mixture was kept at room temp. for 4 hr. Work-up gave a product identical to 9 in all respects (mp, UV, 1H NMR, MS).

Acetone of compound C (7). Compound 7 (40 mg) was dissolved in Me2CO-HCl (5 ml) (30 ml Me2CO–1 drop HCl) and kept for 3 days at room temp. Dilation with H2O, removal of the Me2CO, and extraction with EtOAc afforded a residue, which was purified by prep. TLC (C6H6-Me2CO, 4:1). The acetone (21 mg) crystallized as needles (MeOH), mp 108-111°. (Found: C, 66.5; H, 6.0. C22H22O8 requires C, 66.66; H, 6.02%). 1H NMR: see Table 1; MS m/z: 468 [M]+, 453 [M-H]+, 410 [M-H2O]+.

Compound D (11) crystallized from MeOH as needles, mp 240-242°. (Found: C, 65.55; H, 4.85. Calc. for C22H22O8: C, 65.8; H, 4.9%). Identical (mp, UV, 1H NMR, MS) with 7-hydroxy-2',4',5'-trimethoxyisoflavone [4].

Chromatography of fraction I on silica gel (C6H6-Me2CO, 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 (C6H6-Me2CO or C6H6-CH2Cl2). It was readily identified as amorphigenin (1).

Compound B (2) was obtained as an amorphous solid on rechromatography on silica gel (C6H6-Me2CO, 8:1; [α]D = -159.4° (c 0.5; MeOH). (Found: C, 64.5; H, 5.2. Calc. for C22H22O8: C, 64.78; H, 5.2%). UV λmax MeOH nm: 236 (8000), 244 sh (14400), 292 (19000). Compound B (2) (50 mg) was dissolved in AcO-C2H5N (10:1) and left at room temp. for 12 hr. Usual work-up followed by purification on prep. TLC (C6H6-Me2CO, 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° for 2 hr, then diluted and extracted with CHCl3, afforded 6a,12a-dehydroamorphigenin (5), which crystallized (MeOH) as yellow needles, mp 204-210° (dec.). UV λmax nm (ε): 236 (30 900), 279 (24 300), 308 (19 000); MS m/z: 408 [M]+. 1H NMR: see Table 1.

Acetylation of (Ac2O-C2H5N, 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 NaBH4 (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 (C6H6-Me2CO, 2:1). The reduction product (8) crystallized as prisms (MeOH) of 12α-dihydrodaldinol, mp 120-125°. (Found: C, 64.37; H, 5.5. C22H22O8 requires: C, 64.48; H, 5.6%). [α]D = -178.2° (c 0.5; MeOH); MS m/z: 428 [M]+ (C22H22O8). The O-diaceate (54 mg) prepared from 2 (60 mg) with Ac2O-C2H5N was purified by prep. TLC (C6H6-Me2CO, 4:1). 1H NMR: see Table 1.

Compound C (7) was purified by rechromatography on silica gel (C6H6-Me2CO, 7:1 → 5:1) and gave an amorphous solid. (Found: C, 64.56; H, 5.6. C23H22O8 (as above) Acetylation of 7 (100 mg) afforded after CC (silica gel) (C6H6-Me2CO, 10:1) a diacetate (50 mg) and a triacetate (15 mg) as shown by 1H NMR (Table 1).

Dalbino A (8) was isolated as a crystalline solid (MeOH), mp 152-156° (lit. [5] mp 141-142°). 1H NMR: 52.02 (s, 3 OAc), 2.07 (s, 3 OAc), 2.16 (s, OAc).

Compound G (14), amorphous solid. (Found: C, 59.0; H, 5.6. C23H22O8 requires: C, 58.97; H, 5.8%). UV λmax MeOH nm: 278; MS m/z: 572 [M–H2O]+, 412, 410, 381, 208 (C11H12O4) (base peak), 1H NMR: (CD3)2SO, δ 3.54 (s), 3.63 (s, 2×OMe), 5.73 (d, H-12a, J = 1.0 Hz), 6.43 (d, H-10, J = 8 Hz), 6.62 s, H-11), 7.35 (dd, H-11, J = 8 Hz) 7.38 (s, H-1).
Fraction IV and V
Silica gel
CHCl₃ – MeOH
15:1 → 8:1

Subfraction I
Silica gel
[ CHCl₃ – MeOH – H₂O, 7:2:1 (bottom layer) ]

Subfraction II
(Cryst. MeOH)
compounds IV and V
Silica gel
CHCl₃ – MeOH
15:1 – 8:1

Subfraction III
(Cryst. MeOH, 10:1)

Subfraction IV
Polyamide (H₂O)

Subfraction V
Silica gel
(CHCl₃ – MeOH, 7:2:1)

Subfraction VI
Silica gel
(CHCl₃ – MeOH, 10:1)

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

Acetylation (Ac₂O–C₅H₅N, 10:1) afforded a pentaacetate as needles, mp 175–180°C (CHCl₃–MeOH). (Found: C, 58.25; H, 5.3.
C₃₂H₄₄O₁₈ requires: C, 58.5; H, 5.5) MS m/z: 740 [M–60]+.

'H NMR: δ 2.02 (s, 3 x OAc), 2.08 (s, 2 x OAc), 3.80 (s, 2 x OMe), 6.30 (d, H-11, J = 9 Hz), 6.37 (s, H-4 and H-12), 6.74 (s, H-1), 6.97 (d, H-10, J = 9 Hz).

Oxidation of 14 (100 mg) in MeOH (5 ml) with HIO₄. 2H₂O (40 mg) in H₂O (2 ml) for 2 hr at room temp. yielded a ppt. of 15 which crystallized from MeOH as prisms, mp 139–141°C. (Found: C, 59.3; H, 5.2. C₂₉H₃₂O₁₂ requires: C, 59.18; H, 5.5). MS m/z: 588 [M]+.

'H NMR: δ 3.01 (s, 2 x OAc), 2.04 (s), 2.08 (s), 2 x OAc), 3.86 (s), 3.82 (s, 2 x 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).

Acetylation (Ac₂O–C₅H₅N, 10:1) of 15 gave a tetraacetate as prisms (MeOH), mp 104–106°C. (Found: C, 59.0; H, 5.2. C₂₉H₃₂O₁₂ requires: C, 59.0; H, 5.2). MS m/z: 658 [M]+.

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°C for 1 day. The reaction mixtures were extracted with EtOAc. The organic extracts were washed, dried and evaporated. The residues were purified on columns of silica gel. The aglycones 1, 2, 7 and 11 were obtained (identical mp, TLC and 'H NMR).

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