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NEW METABOLITES FROM *PSOROSPERMUM TENUIFOLIUM**

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Key Word Index—*Psorospermum tenuifolium*; Guttiferae; prenylated bianthrones; 10-isoprenylemodin-anthran-10-ol; anthraquinone.

Abstract—Two prenylated bianthrones, an anthran-10-ol and a new emodin derivative were isolated for the first time from the root bark of *Psorospermum tenuifolium*, together with several known metabolites typical of the genus.

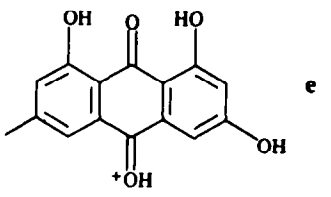
INTRODUCTION

The genus *Psorospermum* is a source of vismiones and other biogenetically linked anthranoids, which show cytotoxic activity [1–3] and feeding deterrence [1]. Following our chemosystematic investigation on the secondary metabolites of the tribe Vismieae (Hypericoideae), we report on our examination of the root bark of *Psorospermum tenuifolium*, collected in Nigeria.

RESULTS AND DISCUSSION

Acetylvismione D (**1**) [4] and vismione D (**1a**) [5] are the main components of the cold acetone extract of *P. tenuifolium* (~ 25 and 8‰, respectively). Vismiones usually co-occur with the corresponding anthrones, bianthrones and anthraquinones, which are at least partially their transformation products formed during the isolation [6]. 3-Geranyloxychrysophanol (the geranyl ether of emodin) and the corresponding 9-anthrone were isolated again, as well as bianthrone A1 (**2**) [7]. Vismione H (**1b**) [8], where a prenyl chain is present instead of the geranyl one, was isolated as a minor component (3%). Madagascin (the prenyl ether of emodin) and its 9-anthrone were found as expected.

Two new bianthrones were also obtained and assigned structures **3** and **4** and the names bianthrone A2a and A2b. The two compounds $C_{45}H_{46}O_8$ and $C_{40}H_{38}O_8$, respectively, showed spectral (^{1}H NMR, UV and IR) data and chemical behaviour very close to those of bianthrone A1. In Table 1 a comparison of the mass fragmentation ions of bianthrones A1, A2a and A2b is presented. The loss of a geranyl chain (as $C_{10}H_{16}$) from $[M]^+$ was seen in the spectrum of **2**, the loss of a prenyl chain (as C_5H_8) in that of **4** and the losses of a geranyl chain and a prenyl chain in



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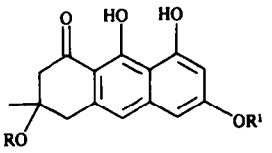
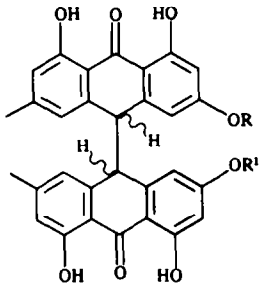
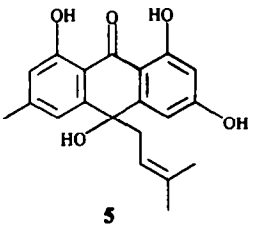


	R	R¹
1	Ac	Geranyl
1a	H	Geranyl
1b	Ac	Prenyl



	R	R¹
2	Geranyl	Geranyl
3	Geranyl	Prenyl
4	Prenyl	Prenyl



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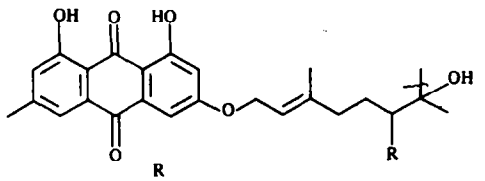

	R
6	H
7	OH

*Part 5 in the series 'Chemistry of *Psorospermum* genus', for part 4 see ref. [4]. A preliminary report was presented at the International Symposium on the Chemistry of Natural Products, Edmonton, Canada, 23–26 June 1985.

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Table 1. Mass fragmentation of bianthrones A1, A2a and A2b

	A1 (2)	A2a (3)	A2b (4)
$[M]^+$	782 (17)*	714 (2)	646 (2)
$[M-C_{10}H_{16}]^+$	646 (3)	578 (2)	
$[M-C_5H_9]^+$		646 (1)	578 (2)
$[a]^+$	510 (9)	510 (2)	510 (2)
$[b]^+$	392 (15)	392 (17)	
$[c]^+$		324 (42)	324 (72)
$[d]^+$	256 (100)	256 (100)	256 (100)

*m/z (rel. int.)

Table 2. ^{13}C NMR spectra of anthraquinones 6 and 7 ($CDCl_3$)

C	6[2]	7
1	166.2	165.7
1a	110.3	110.1
2	108.9	108.6
3	162.8	162.4
4	107.8	107.6
4a	133.6	133.1
5	118.7	118.7
5a	135.5	135.1
6	148.5	148.3
7	124.6	124.4
8	165.4	165.0
8a	114.0	113.6
9	191.0	190.6
10	182.2	182.0
11	22.1	221
12	66.0	65.8
13	121.3	121.2
14	142.7	142.3
15	16.7	16.7
16	39.9	36.5
17	22.3	23.2
18	43.5	77.8
19	70.9	73.1
20	30.0	29.3
21	29.4	26.4

that of 3. The losses of both the 3- and 3'-*O*-substituents gave in each case the ion $[a]^+$, corresponding to the molecular ion of emodinbianthrone. Moreover bianthrone A1 gave the ion $[b]^+$, corresponding to the molecular ion of the geranyl ether of emodinanthrone, whereas bianthrone A2b gave ion $[c]^+$, corresponding to the molecular ion of the prenyl ether of emodinanthrone. Notably bianthrone A2a showed both peaks $[b]^+$ and $[c]^+$. In all the cases the base peak, $[d]^+$, corresponded to the molecular ion of emodinanthrone. Both compounds 3 and 4 on acid treatment gave emodin bianthrone, as a mixture of *meso* and (±) forms, as did bianthrone A1 [7]. The structures 3 and 4 are in agreement with the co-occurrence of the component anthrones.

Acetylvismione F [9], vismione F [7] and emodin were also isolated and identified by comparison with authentic samples. The low intensity molecular peak (2% at *m/z* 340) in the EIMS spectrum of a new pigment $C_{20}H_{20}O_5$, 5, was confirmed in the CIMS spectrum (base peak at *m/z* 341). Its ^1H NMR spectrum showed a close similarity with that of emodin in the aromatic region as well as the presence of two chelated hydroxyl groups. In addition the signals of a γ,γ'-dimethylallyl chain were displayed, and the chemical shifts suggested a link with an sp_3 carbon. Only the absorbance of a chelated CO was present in the carbonyl region of the IR spectrum and accordingly the UV spectrum showed the presence of a chromophore less extended than in anthraquinones of the emodin type (λ_{max} ~ 430 nm) and comparable with those of xanthones or benzophenones (λ_{max} ~ 360 nm). These data and the existence of an undetermined oxygen (from the molecular formula) are consistent with the structure of a 10-isoprenylemodinanthran-10-ol (5). Notably in the mass spectrum the loss of the prenyl chain (as C_5H_9) from $[M]^+$ gave rise to the oxonium ion *e*, $C_{15}H_{11}O_5$ (base peak).

The emodin derivative $C_{25}H_{28}O_6$, 6, also present in the extract, has been reported from *Psorospermum febrifugum* [2]. We have now isolated a more polar pigment $C_{25}H_{28}O_7$, 7, closely related to 6. The ^1H NMR (in the aromatic region) and UV-VIS spectra were coincident and the difference between the two compounds, ie the extra oxygen of 7, was localized on the C_{10} chain. In the mass spectrum of 7 the loss of the C_{10} chain gave the base peak as in those of 6 and 3-geranyloxyemodin. A broad triplet (1H) at δ3.83 suggested the presence of a $CH_2\underline{CH}(OH)$ group in 7, while the comparison (Table 2) between the ^{13}C NMR spectra of the two compounds was conclusive. The close coincidence of the carbon signals was perturbed at the level of C-16 and C-18 was thought to bear the new oxygen by its large paramagnetic shift to δ77.8. The smaller downfield shifts of C-17 and C-19 and upfield shifts of C-16, C-20 and C-21 were in agreement with the introduction (β and γ effects) of an oxygen in C-18 [10]. Thus structure 7 was assigned to the last new metabolite.

EXPERIMENTAL

Plant material. Roots of *P. tenuifolium* were collected in Nigeria by one of us (J.U.O.). A voucher specimen PST-85 is deposited in the Herbarium of Centro Chimica dei Recettori.

Extraction and fractionation. Air-dried, finely ground bark of roots (310 g) was extracted exhaustively with cold Me_2CO, the pooled extracts giving a residue of 50 g. CC of a part of the extract (10 g) on silica gel eluted with CH_2Cl_2–EtOAc mixtures afforded nine fractions (PT1–PT9) which on further purification yielded: 3-geranyloxychrysophanol [5] (100 mg, mp 124–126°) from PT1 (crystallization from Et_2O); 3-geranyloxychrysophanol (230 mg) and madagascin [11] (140 mg, mp 157–158°) from PT2 (silica gel; C_6H_6–hexane, 2:1); 3-geranyloxy-6-methyl-1,8-dihydroxyanthraquinone [12] (120 mg, mp 98–99°), madagascinanthrone [11] (60 mg, mp 163–164°), friedelin (60 mg), bianthrone A1 [7] (2, 50 mg, mp 134–136°), bianthrone A2a (3, 120 mg) and bianthrone A2b (4, 30 mg) from PT3 (silica gel; C_6H_6–hexane, 3:1, and C_6H_6); acetylvismione D [4] (1, 2.5 g, mp 65–66°) from PT4 (silica gel; CH_2Cl_2); vismione H [8] (260 mg, mp 109–112°) from PT5 (silica gel; CH_2Cl_2); acetylvismione F [9] (150 mg, mp 118–120°) from PT6 (silica gel; CH_2Cl_2–EtOAc, 19:1); emodin (350 mg), 3-(18,19-dihydro-19-hydroxygeranyloxy)-6-methyl-1,8-dihydroxyanthraquinone [2] (6, 80 mg, mp 105–106°), betulin (30 mg) and 10-isopentenylemodinanthran-10-ol (5, 25 mg) from PT7 (silica gel; CH_2Cl_2–EtOAc, 9:1); vismione D [5] (2, 800 mg, mp 142–144°) and vismione F [7]

(120 mg, mp 144–145°) from PT8 (silica gel; hexane–EtOAc, 3:2); 3-(18, 19-dihydro-18, 19-dihydroxygeranyloxy)-6-methyl-1,8-dihydroxyanthraquinone (**6**, 40 mg) from PT9 (PLC silica gel; hexane–EtOAc, 3:2). The known compounds were identified by comparison (spectral data, co-TLC and mmp) with authentic samples.

Bianthrone A2a (**3**). $C_{45}H_{46}O_8$ (Found: C, 76.0; H, 6.2%. Calc.: C, 75.6; H, 6.4%); mp 81–83° (Et_2O–hexane); $\alpha_D = 0°$; UV λ_{max}^{EtOH} nm: 280, 362; ^{1}H NMR ($CDCl_3$): δ 12.23, 12.15, 11.96, 11.88 (1H each, *s*, 1-OH, 1′-OH, 8-OH, 8′-OH), 6.68 (2H, *br s*, H-5, H-5′), 6.36 (2H, *br s*, H-4, H-4′), 6.08 (2H, *br s*, H-7, H-7′), 5.98 (2H, *br s*, H-2, H-2′), 5.45 (2H, *br t*, J = 7 Hz, 2 × CH=), 5.10 (1H, *m*, CH=), 4.55 (4H, *br d*, J = 7 Hz, 2 × OCH_2), 4.28 (2H, *br s*, H-10, H-10′), 2.33, 2.29 (3H each, *s*, 6-Me, 6′-Me), 2.3 ÷ 2.1 (8H, *m*, 4 × CH_2), 1.79 (9H, *br s*, 3 × Me), 1.73, 1.67 (3H each *s*, 2 × Me); EIMS (probe) 70 eV: Table 1. Bianthrone A2a (80 mg) was refluxed for 1 h in 3M HCl. Standard work-up and purification on silica gel ($CHCl_3$–MeOH, 49:1) gave 10,10′-emodinbianthrone (25 mg) as a 1:1 mixture of *meso* and (±) diastereoisomers, identified by comparison with an authentic specimen [7].

Bianthrone A2b (**4**). $C_{40}H_{38}O_8$ (Found: C, 74.9; H, 5.8%. Calc.: C, 74.3; H, 5.9; mp 178–179° (Et_2O–hexane); $\alpha_D = 0°$; λ_{max}^{EtOH} nm: 280, 362; ^{1}H NMR ($CDCl_3$): δ 12.17, 12.09, 11.85, 11.80 (1H each, 1-OH, 1′-OH, 8-OH, 8′-OH), 6.68 (2H, *br s*, H-5, H-5′), 6.33 (2H, *br s*, H-4, H-4′), 6.08 (2H, *br s*, H-7, H-7′), 5.97 (2H, *br s*, H-2, H-2′), 5.45 (2H, *br t*, J = 7 Hz, 2 × CH=), 4,48 (2H, *br d*, J = 7 Hz, 2 × OCH_2), 4.28 (2H, *br s*, H-10, H-10′), 2.32, 2.29 (3H each, *s*, 6-Me, 6′-Me), 1.83 (12H, *br s*, 4 × Me); EIMS (probe) 70 eV: Table 1. Bianthrone A2b (65 mg) gave 10,10′-emodinbianthrone (20 mg) under the same conditions as those described for its formation from bianthrone A2a.

10-*Isopentenylemodinanthran*-10-*ol* (**5**). $C_{20}H_{20}O_5$, $[M]^+$ found 340.1300, calcd 340.1310; mp 190–192° (MeOH); UV λ_{max}^{EtOH} nm (log ε): 258 (3.63), 274 (3.68), 368 (3.83); λ_{max}^{NaOAc}: 258, 268, 390; ^{1}H NMR (CD_3COCD_3): δ 12.33, 12.15 (1H each, *s*, 1-OH, 8-OH), 7.25 (1H, *d*, J = 1.5 Hz, H-5), 7.0 (1H, *d*, J = 2 Hz, H-4), 6.65 (1H, *d*, J = 1.5 Hz, H-7), 6.28 (1H, *d*, J = 2 Hz, H-2), 4.60 (1H, *m*, CH=), 2.55 (2H, *d*, J = 7 Hz, CH_2), 2.40 (3H, *s*, 6-Me), 1.45, 1.02 (3H each, *br s*, 2 × Me); IR ν_{max}^{KBr} cm^{-1}: 3420, 3360, 1636, 1612, 1595; EIMS *m/z* (rel. int.): 340 $[M]^+$ (2), 271 (Found 271.0616, calcd for $C_{15}H_{11}O_5$, 271.0606) $[M-C_5H_9]^+$ (100), 270 (15), 256 (4), 229 (15), 201 (8), 69 (16), 41 (12); m*: 216.0 (340 → 271), 193.5 (271 → 229), 176.4 (229 → 201); CIMS *m/z* (rel. int.): 341 $[M+H]^+$ (100), 325 $[M-Me]^+$ (28), 323 (15), 271 $[M-C_5H_9]^+$, 260 (22), 257 (25), 256 (10).

3-(18,19-*Dihydro*-18,19-*dihydroxygeranyloxy*)-1,8-*dihydroxy*-6-*methylanthraquinone* (**6**). $C_{25}H_{28}O_7$, $[M]^+$ found 440.1835, calcd 440.1835; mp 80–82° (EtOH); UV λ_{max}^{EtOH} nm (log ε): 253 (4.10), 266 (4.12), 285 (4.10), 436 (3.93); IR ν_{max}^{KBr} cm^{-1}: 3420, 1670, 1625, 1605, 1560; ^{1}H NMR (Me_2CO-d_6): δ 12.0, 11.83 (1H each, *s*, 1-OH, 8-OH), 7.35 (1H, *d*, J = 1.8 Hz, H-5), 7.05 (1H, *d*, J = 2.5 Hz, H-4), 6.95 (1H, *d*, J = 1.8 Hz, H-7), 6.57 (1H, *d*, J = 2.5 Hz, H-2), 5.60 (2H, *br*, 2 × OH), 5.50 (1H, *br t*, J = 6.5 Hz, CH=), 4.70 (2H, *d*, J = 6.5 Hz, OCH_2), 3.83 (1H, *br t*, J = 6 Hz, 18-H), 3.50 ÷ 2.80 (4H, *m*, 2 × CH_2), 2.37 (3H, *br s*, 6-Me), 1.81 (3H, *br s*, 14-Me), 1.11 (6H, *s*, 20-Me, 21-Me); ^{13}C NMR: see Table 2; EIMS *m/z* (rel. int.): 440 $[M]^+$ (8), 422 $[M-H_2O]^+$ (2), 382 $[M-C_3H_6O]^+$ (3), 323 $[382-C_3H_7O]^+$ (4), 321 (6), 295 (4), 284 (5), 283 (6), 270 $[M-C_{10}H_{18}O_2]^+$ (100), 256 (10), 242 (8), 241 (6), 229 (2), 213 (4), 153 $[C_{10}H_{17}O]^+$ (7), 59 $[C_3H_7O]^+$ (18).

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