

PRENYLATED ANTHRANOIDS FROM *PSOROSPERMUM* SPECIES*

F. DELLE MONACHE,† B. BOTTA, G. DELLE MONACHE and G. B. MARINI BETTOLO

Centro Chimica dei Recettori del C.N.R., c/o Istituto di Chimica, Università Cattolica, Via Pineta Sacchetti 644, 00168 Rome, Italy

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Key Word Index—*Psorospermum glaberrimum*; *P. corymbiferum*; Guttiferae; Vismieae; geranylmodin anthrone; emodin; vismiones C, D, F and G; acetylvismione F.

Abstract—The chemical composition of the root extracts of two *Psorospermum* sp. from the Ivory Coast is reported. Together with previously known compounds, acetylvismione F and 2-geranylmodin anthrone were isolated from *P. corymbiferum*, and vismione G from *P. glaberrimum*. Geranyl substitution is confirmed to be a typical feature of this genus.

INTRODUCTION

The tribe Vismieae (subfamily Hypericoideae) has been divided by Engler [1] into three genera; *Vismia*, *Harungana* and *Psorospermum*. Our previous studies have shown the presence of prenylated anthranoids both in the South American *Vismia* [2] and in the African *Psorospermum* genera [3–5]. In view of the chemotaxonomic value and biological (cytotoxic and antifeeding) activities of these compounds, we have examined other *Psorospermum* sp. This paper deals with the constituents of the root extracts of *P. glaberrimum* and *P. corymbiferum*.

RESULTS AND DISCUSSION

The root bark extract of *P. glaberrimum* yielded seven compounds, six of which were identified as 3-geranyloxyemodin, 2-isoprenylemodin, emodin and the vismiones C, D (1) and F (2) by comparison with authentic samples. This is the first report of emodin from Vismieae, whereas the other pigments have been isolated from the fruit [3] or the root bark [4, 5] of *P. febrifugum*.

The new pigment, $C_{27}H_{32}O_6$, showed spectral data (see Experimental) which closely resembled those of the previously known 6-*O*-acetylated vismiones. It was named vismione G. In particular, the non-equivalence of the protons of the C-5 and C-7 methylene signals and the downfield shift of the Me-6 signal in the 1H NMR spectrum, and the loss of 60 mass units from the molecular ion in the mass spectrum placed the acetoxy group on C-6. The 1H NMR spectrum also showed the signals of a C-geranyl side chain, which was placed on C-10 by the presence of the signals of two *meta*-coupled aromatic protons. Consequently, vismione G was assigned struc-

ture 3. The biogenetic derivation of vismiones G (3) and F (2) from vismione D (1) is evident.

In addition to 3-geranyloxyemodin and vismiones D and F, two new compounds were isolated from the root bark of *P. corymbiferum*. The first compound (M , 392) was identified as the anthrone, 4, which was easily oxidized to the known [4] anthraquinone, 5, on standing in solution. The second compound, $C_{27}H_{32}O_6$ (M , 452), for the same reasons as those given above for 3, was found to be a vismione with an OAc-6 group. The aromatic proton signals in the 1H NMR spectrum indicated the same substitution pattern as vismione F (2). Moreover, the new compound on silica gel yielded the same transformation products as 2. The compound was, thus, assigned structure 6 and the name acetylvismione F.

The mass fragmentation patterns of the isomeric $[M]^+$ 452 vismiones, 3 and 6, need further comment. The different locations of the geranyl side chain on C-10 (3) and on C-2 (6) lead to quite distinct behaviours in the mass spectrometer. In both cases, the initial loss of acetic acid from $[M]^+$ gives an ion at m/z 392, which is probably rearranged to the anthrone form [2]. This seems to be confirmed by the successive loss of $C_{10}H_{16}$ in 3, typical of an aliphatic geranyl chain, whereas in 6 only the loss of an aromatic geranyl chain (as a C_9H_{15} fragment) is observed. These findings confirm that *Psorospermum* and *Vismia* produce prenylated anthranoids with distinct substituents in the two genera, i.e. C_{10} and C_5 side chains, respectively.

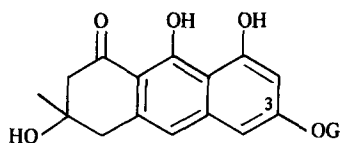
EXPERIMENTAL

Plant material. The roots of *P. glaberrimum* Hochr. and *P. corymbiferum* Hochr. were collected near Sinematiali village (between Ferkessedougou and Korhogo, north Ivory Coast) by Professor P. Garnier (Aubagne, France) in August 1983 and identified by Dr. H. Tébé (Orstom, Adiopodoumé, Ivory Coast). Voucher specimens are deposited at the herbarium of Centro Chimica Recettori under the cipher PG 1983(R) and PC 1983 (R), respectively.

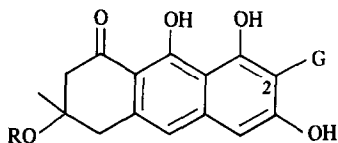
Isolation of the constituents of *P. glaberrimum*. Air-dried finely ground root bark (30 g) was extracted twice with cold Me_2CO

*Part 3 in the series "Chemistry of *Psorospermum* genus" For Part 2, see ref. [4]

†To whom correspondence should be addressed.

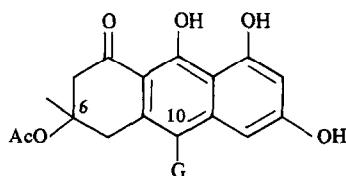


1

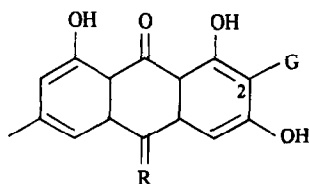


2 R = H

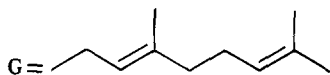
6 R = Ac



3

4 R = H₂

5 R = O



The residue (4.8 g) of the pooled extracts was chromatographed on silica gel to give five fractions: G₁ (185 mg; CHCl₃), G₂ (167 mg; CHCl₃), G₃ (685 mg; CHCl₃-MeOH, 19:1), G₄ (385 mg; CHCl₃-MeOH, 19:1) and G₅ (1.04 g; CHCl₃-MeOH, 19:1). Further purification yielded: geranyloxyemodin (105 mg) from G₁ (silica gel; hexane-EtOAc, 4:1); 2-isoprenylemodin (250 mg), vismione C (32 mg) and emodin (70 mg) from G₃ (silica gel; hexane-EtOAc, 4:1, followed by prep. TLC in C₆H₆-EtOAc, 17:3); emodin and vismione G from G₄ (prep. TLC; C₆H₆-EtOAc, 17:3); and vismiones D (210 mg) and F (380 mg) from G₅ (silica gel; C₆H₆-EtOAc, 4:1). Fraction G₂ (unidentified pigment) was not processed.

Isolation of the constituents of *P. corymbiferum*. Root bark (17 g) was extracted as above. The residue (3 g) on silica gel gave five fractions: C₁ (160 mg; CH₂Cl₂), C₂ (290 mg; CHCl₃), C₃ (370 mg; CHCl₃), C₄ (1.06 g; CHCl₃-MeOH, 19:1) and C₅ (395 mg; CHCl₃-MeOH, 9:1). Further purification yielded geranyloxyemodin (70 mg) from C₁; 2-geranylemodin anthrone

(55 mg) from C₂ (prep. TLC; hexane-EtOAc, 4:1); and acetylvismione F (205 mg) from C₃ (prep. TLC; hexane-EtOAc, 4:1, two runs). Fractions C₄ (impure acetylvismione F) and C₅ (mixture of vismiones D and F) were not processed. All the previously known compounds were identified by comparison (mp, TLC and ¹H NMR spectrum) with authentic specimens.

Vismione G (3). Mp 185–188° (dec.) (red solid, Et₂O-hexane). (Analysis: C, 71.86; H, 7.05. C₂₇H₃₂O₆ requires: C, 71.66; H, 7.13%). UV λ_{CHCl₃} nm (log ε): 278, 324 sh, 408 (4.33, 3.60, 3.74); IR ν_{CHCl₃} cm⁻¹: 3580, 3400, 1725, 1626, 1603; ¹H NMR (60 MHz; Me₂CO-d₆): δ 16.9 (1H, s, OH-9), 10.2 (1H, s, OH-1), 9.2 (1H, br s, OH-3), 6.75 (1H, d, J = 2 Hz, H-4), 6.42 (1H, d, J = 2 Hz, H-2), 5.30 (1H, t, J = 7 Hz), 5.0 (1H, br t), 3.75 and 3.30 (1H each, d, J = 16 Hz, CH₂-5), 3.45 (2H, d, J = 7 Hz), 3.10 (2H, br s, CH₂-7), 2.15 (4H, br), 1.75 (6H), 1.67 (9H); EIMS (probe) 70 eV, m/z (rel. int.): 452 [M]⁺ (1), 392 [M - HOAc]⁺ (2), 270 [392 - C₉H₁₄]⁺ (38), 256 [392 - C₁₀H₁₆]⁺ (100), 227 (15), 137 (20), 135 (15).

2-Geranylemodin anthrone (4). ¹H NMR (60 MHz; Me₂CO-d₆): δ 12.85 (1H, s, OH), 12.27 (1H, s, OH), 9.40 (1H, s, OH-3), 6.67, 6.57 and 6.50 (1H each, s, H-4, H-5, H-7), 4.90–5.35 (2H, m), 4.15 (2H, s, CH₂-10), 3.35 (2H, d, J = 7 Hz), 2.30 (3H, s), 2.0 (4H, m), 1.80, 1.62, 1.58 (3H each, s); EIMS (probe) 70 eV, m/z (rel. int.): 392 [M]⁺ (74), 349 (18), 337 (10), 323 (98), 269 [M - C₉H₁₅]⁺ (100), 256 (30). Attempts to crystallize resulted in air oxidation to the corresponding anthraquinone [4].

Acetylvismione F (6). Mp 119–121° (dec.) (red-brown solid, Et₂O-hexane). (Analysis: C, 71.80; H, 7.10. C₂₇H₃₂O₆ requires: C, 71.66; H, 7.13%). UV λ_{CHCl₃} nm (log ε): 277, 322, 334 sh, 407 (4.33, 3.80, 3.74, 3.87); IR ν_{CHCl₃} cm⁻¹: 3550, 3390, 1730, 1630, 1605; ¹H NMR (60 MHz; Me₂CO-d₆): δ 16.40 (1H, s, OH-9), 10.0 (1H, s, OH-1), 9.30 (1H, br s, OH-3), 6.73 (1H, s, H-10), 6.65 (1H, s, H-4), 5.35 (1H, t, J = 10 Hz), 5.10 (1H, br t), 3.65 and 3.10 (1H each, d, J = 16 Hz, CH₂-5), 3.45 (2H, d, J = 7 Hz), 3.05 (2H, br s, CH₂-7), 2.0–2.20 (4H, m), 1.83, 1.78, 1.68, 1.60, 1.55 (3H each, s); EIMS (probe) 70 eV, m/z (rel. int.): 452 [M]⁺ (3), 392 [M - HOAc]⁺ (75), 349 (18), 337 (10), 323 (98), 269 [392 - C₉H₁₅]⁺ (100). Acetylvismione F on silica gel (1 day) gave a mixture of 2-geranylemodin anthrone and anthraquinone.

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