Phytochemistry, Vol. 25, No. 5, pp. 1217–1219, 1986.
Printed in Great Britain.

0031–9422/86 $3.00 + 0.00

VISMIONE H AND PRENYLATED XANTHONES FROM *VISMIA GUINEENSIS**

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

Centro Chimica dei Recettori del CNR, c/o Istituto di Chimica, Università Cattolica, Via della Pineta Sacchetti 644, 00168 Rome, Italy; ‡Dipartimento di Chimica, Università della Calabria, Arcavacata di Rende (Cs), Italy

(*Revised received* 26 *September* 1985)

Key Word Index—*Vismia guineensis*; Guttiferae; Vismieae; vismione H; prenylated xanthones.

Abstract—The root bark of *Vismia guineensis*, collected on the Ivory Coast, contained the known geranyloxyemodin, geranyloxyemodin anthrone, madagascin anthrone, bianthrone A_1 and five new compounds: vismione H and the prenylated xanthones V_1, V_2, V_{1a} and V_{2a}.

INTRODUCTION

In a systematic study on the tribe Vismieae (subfamily Hypericoideae), we found vismiones with C_5 substituents in the South American *Vismia* and, by contrast, vismiones with geranyl chains in the African sister genera, *Psorospermum* [2]. We report now the results from the examination of a *Vismia* sp., growing in West Tropical Africa [3, 4], i.e. *V. guineensis* (L.) Choisy, a small tree whose roots and bark are used as a tropical remedy for skin diseases [5]. A previous paper [6] on this species reported only on the composition of the essential oil.

RESULTS AND DISCUSSION

The acetone extract of the root bark yielded the previously known 3-geranyloxyemodin, 3-geranyloxyemodin anthrone, madagascin anthrone, bianthrone A_1 [7] and five new pigments, whose separation is described in the Experimental.

The first pigment, $C_{22}H_{24}O_6$, showed the typical features of an acetylvismione [8] and was assigned the structure **1** and the name vismione H. The presence of a 3-*O*-prenyl group was inferred by the ^{1}H NMR spectrum, which also contained the signals of three aromatic protons, two of which were *meta* coupled. The loss of 68 amu from both the $[M]^+$ and $[M - AcOH]^+$ ions in the mass spectrum supported the assignment. The UV and IR spectra of each of the other four pigments showed the presence of a xanthone nucleus [9]. The substitution patterns of the pigments were as shown in structures **2**–**5**. The main component, **2**, $C_{23}H_{22}O_6$ (M^+ 394), namely xanthone V_1, gave a dimethyl and a triacetyl derivative, which accounted for the presence of three hydroxyls, one of which was hydrogen bonded. The other substituents were identified by ^{1}H NMR as being a 3,3-dimethylallyl side chain, a 2,2-dimethyl-2H-pyran ring and two *ortho* coupled aromatic protons. A bathochromic shift with sodium acetate and sodium acetate–boric acid in the UV spectrum fixed the two unchelated hydroxyls on C-5 and C-6. Therefore both the C_5 substituents were placed on ring A. The angular closure of the pyran ring was supported by the formation only of an addition product, **7**, with trifluoroacetic acid and by the close similarity of the ^{13}C NMR data of **2** with those of the isomeric macluraxanthone (**6**) (Table 1).

Compound **3**, $C_{24}H_{24}O_7$ (M^+ 424), namely xanthone V_2, showed a ^{1}H NMR spectrum similar to that of **2** except for the presence of signals due to an additional methoxyl group, which was placed on C-7 out of consideration of the chemical shift [10] of the single aromatic proton. The ^{13}C NMR data, particularly the chemical shift of the methoxyl [11], confirmed the assignment and the structure **3**.

In xanthone V_{1a} (**4**, M^+ 396) the 2,2-dimethyl-2H-pyran ring of **2** was substituted with a 3,3-dimethylallyl side chain (^{1}H NMR evidence); the same relationship was noted between xanthone V_{2a} (**5**, M^+ 426) and **3**. Therefore xanthones V_{1a} and V_{2a} were assigned the structures **4** and **5**, respectively. This is the first report of prenylated xanthones from the genus *Vismia*, only simple xanthones having been isolated from the South American *Vismia* spp. [12].

EXPERIMENTAL

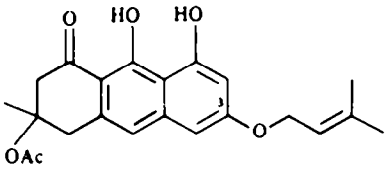
Plant material. The roots of *V. guineensis* were collected on the Ivory Coast in January 1984 and identified by Dr. H. Téhé (ORSTOM, Adiopodoumé, Ivory Coast) and Dr. P. Garnier (Ausbagne, France). A voucher specimen is held by the Herbarium of Centro Chimica dei Recettori under the cipher VG 1984 (R).

Isolation of the constituents. Air dried finely ground root bark (100 g) was extracted with cold Me_2CO (× 2). The residue (7.5 g) of the pooled extracts was chromatographed on silica gel ($CHCl_3$–MeOH, 50:1) to give three fractions; VG_1 (600 mg), VG_2 (650 mg) and VG_3 (4 g).

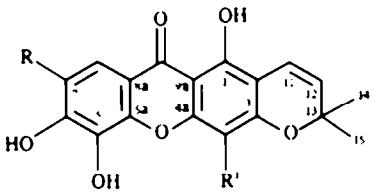
Further purification yielded geranyloxyemodin (300 mg) from VG_1 (silica gel; hexane–EtOAc, 9:1); geranyloxyemodin anthrone (50 mg), madagascin anthrone (75 mg), bianthrone A_1

*Part 11 in the series "Chemistry of *Vismia* genus". For part 10 see ref. [1].

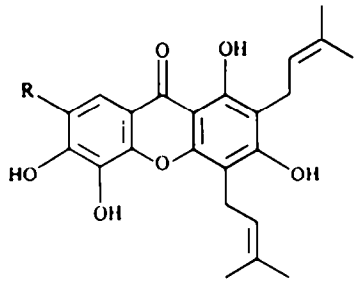
†To whom correspondence should be addressed.



1



	R	R'
2	H	
3	OMe	
6	H	
7	H	



	R
4	H
5	OMe

(170 mg) and β-sitosterol (45 mg) from VG_2 (silica gel; hexane–EtOAc, 9:1 and 4:1); vismione H (310 mg), xanthone V_1 (490 mg), xanthone V_{1a} (85 mg), xanthone V_2 (220 mg) and xanthone V_{2a} (55 mg) from VG_3 (silica gel; C_6H_6–EtOAc, 9:1, 4:1 and 7:3). The last four compounds needed further purification (silica gel; $CHCl_3$). All the previously known compounds were identified by comparison (^{1}H NMR, MS and co-TLC) with authentic samples.

Vismione H (1). Red solid (Et_2O–hexane), mp 110–114° (dec). Found: C, 68.91; H, 6.20; $C_{22}H_{24}O_6$ requires C, 68.76; H, 6.29%. UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 276, 347 sh, 397 (4.74, 4.01, 4.26); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500, 3400, 1725, 1625; ^{1}H NMR (60 MHz, Me_2CO-d_6): δ 16.1 (1H, *s*, OH-9), 9.60 (1H, *s*, OH-1), 6.87 (1H, *s*, H-10), 6.65 (1H, *d*, *J* = 2 Hz, H-4), 6.33 (1H, *d*, *J* = 2 Hz, H-2), 5.45 (1H, *t*, *J* = 7 Hz), 4.60 (2H, *d*, *J* = 7 Hz), 3.68 and 3.20 (1H each, *d*, *J* = 16 Hz, CH_2-5), 3.10 (2H, *s* (*br*), CH_2-7), 1.77 (6H, *s*), 1.68 (3H, *s*); EIMS (probe) 70 eV, *m/z* (rel. int.): 384 $[M]^+$ (6), 324 $[M-AcOH]^+$ (25), 316 $[M-C_5H_8]^+$ (3), 256 $[324-C_5H_8]$ (100), 227 (20); m* 273.4 (384 → 324) and 202.3 (324 → 256).

Xanthone V_1 [*1,5,6-trihydroxy-6',6'-dimethyl-2H-pyrano-(2',3':3,2)-4-(3,3-dimethylprop-2-enyl) xanthone*] (2). Red-brown solid (Et_2O), mp 214–215°. Found: C, 70.15; H, 5.55; $C_{23}H_{22}O_6$ requires C, 70.04; H, 5.62. UV λ_{max}^{MeOH} nm (log ε): 240, 285, 337, 380 sh (4.31, 4.66, 4.31, 3.76); λ_{max}^{NaOAc} nm: 284, 368; $\lambda_{max}^{NaOAc+H_3BO_3}$ 284, 349; $\lambda_{max}^{AlCl_3}$ 260 sh, 307, 400; $\lambda_{max}^{AlCl_3+HCl}$ 255 sh, 301, 367. IR ν_{max}^{KBr} cm^{-1}: 3400, 1620, 1580; ^{1}H NMR (60 MHz, Me_2CO-d_6): δ 13.45 (1H, *s*, OH-1), 7.60 (1H, *d*, *J* = 8.5 Hz, H-8), 6.95 (1H, *d*, *J* = 8.5 Hz, H-7), 6.66 (1H, *d*, *J* = 10 Hz, H-11), 5.66 (1H, *d*, *J* = 10 Hz, H-12), 5.30 (1H, *t*, *J* = 7 Hz), 3.52 (2H, *d*, *J* = 7 Hz), 1.85 [3H, *s* (*br*)], 1.65 [3H, *s* (*br*)], 1.47 (6H, *d*); $\Delta\delta = \delta_{C_5D_5N} - \delta_{Me_2CO\text{-}d_6}$: H-8 (+0.35), H-7 (+0.27), H-11 (+0.27), CH_2-4 (+0.22); ^{13}C NMR: Table 1; EIMS (probe) 70 eV, *m/z* (rel. int.): 394 $[M]^+$ (63), 379 (100), 351 $[M-C_4H_7]^+$ (22), 339 (25), 197 (2), 182 (6), 162 (17). *Dimethyl derivative*: yellow needles (Et_2O hexane), mp 161–163°. UV λ_{max}^{MeOH}: 296, 334 sh, 369, 420 sh; $\lambda_{max}^{AlCl_3}$ 295, 334 sh, 369, 420 sh; $\lambda_{max}^{AlCl_3+HCl}$ 294, 367, 400 sh; ^{1}H NMR (60 MHz, $CDCl_3$): δ 13.1 (OH-1, *s*), 7.82 (H-8, *d*), 6.80 (H-7, *d*), 6.62 (H-11, *d*), 5.53 (H-12, *d*), 5.20 (1H, *t*), 3.97 (6H, *s*), 3.5 (2H, *d*), 1.83 (3H, *s*), 1.66 (3H, *s*), 1.47 (6H, *s*). *Triacetyl derivative*: light yellow needles (Et_2O), mp 197–200°. ^{1}H NMR (60 MHz, Me_2CO-d_6): δ 8.0 (H-8, *d*), 7.25 (H-7, *d*), 6.55 (H-11, *d*), 5.87 (H-12, *d*), 5.25 (1H, *t*), 3.53 (2H, *d*), 2.40 (6H, *s*), 2.33

Table 1. ^{13}C NMR data of compounds **2**, **3** and **6** [25.2 MHz, acetone-d_6 or DMSO-d_6 (**6**), TMS as int. standard]

C	6*[9]	2†	3‡
1	157.7§	158.2§	157.9§
2	103.9‖	104.6‖	104.6‖
3	155.3§	154.5§	154.7§
4	112.5	108.0	107.9
4a	154.4§	156.3§	156.1§
5a	145.6	146.8	142.9¶
5	132.5	133.0	133.9
6	151.3	151.9	141.8¶
7	112.7	114.3	146.1
8	115.3	117.2	96.1
8a	112.5	113.0	112.7
9	180.1	181.1	180.2
9a	102.1‖	102.9‖	103.2‖
11	114.9	115.3	116.1
12	127.1	127.1	127.8
13	77.5	79.2	78.3
14	27.1	29.1	28.2
15	27.1	29.1	28.2

*C-4 chain: δ40.3, 29.3, 29.3, 150.0, 107.2.

†C-4 chain: δ21.6, 123.3, 131.0, 25.7, 17.9.

‡C-4 chain: δ21.7, 123.3, 131.2, 25.7, 17.9; OMe, δ56.2.

§‖¶In the same column, signal having the same symbol may be interchanged.

(3H, *s*), 1.85 (3H, *s*), 1.65 (3H, *s*), 1.47 (6H, *s*). Xanthone V_1 (60 mg) in TFA overnight followed by CC (silica gel, $CHCl_3$) gave **7**, mp 135–136° (Et_2O–hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520, 1770; ^1H NMR (60 MHz, $CDCl_3$): δ13.20 (OH-1, *s*), 7.65 (H-8, *d*), 6.90 (H-7, *d*), 6.67 (H-11, *d*), 5.53 (H-12, *d*), 3.0–2.65 (2H, A_2 part of A_2B_2), 2.30–1.95 (2H, B_2 part of A_2B_2), 1.65 (6H, *s*), 1.47 (6H, *s*).

Xanthone V_2 [1,5,6-*trihydroxy*-7-*methoxy*-6′,6′-*dimethyl*-2H-*pyrano* (2′,3′:3,2)-4-(3,3-*dimethylprop*-2-*enyl*) *xanthone*] (**3**). Orange solid (CH_2Cl_2 hexane), mp 210–213°. Found: C 67.95; H, 5.62; $C_{24}H_{24}O_7$ requires C, 67.91; H, 5.70%. UV λ_{max}^{MeOH} nm (log ε): 289, 339 (4.49, 4.10); λ_{max}^{NaOAc} nm: 287, 387; $\lambda_{max}^{NaOAc + H_3BO_3}$ 293, 364; $\lambda_{max}^{AlCl_3}$ 299, 408; $\lambda_{max}^{AlCl_3 + HCl}$ 298, 371; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520, 1640 1595; ^1H NMR (60 MHz, Me_2CO-d_6): δ13.45 (1H, *s*, OH-1), 7.14 (1H, *s*, H-8), 6.65 (1H, *d*, J = 10 Hz, H-11), 5.65 (1H, *d*, J = 10 Hz, H-12), 5.30 (1H, *t*, J = 7 Hz), 3.90 (3H, *s*), 3.50 (2H, *d*, J = 7 Hz), 1.85 (3H, *s*), 1.65 (3H, *s*), 1.48 (6H, *s*); $\Delta\delta = \delta_{C_5D_5N} - \delta_{Me_2CO\text{-}d_6}$: H-8 (+0.40), H-11 (+0.36), CH_2-4 (+0.28); ^{13}C NMR: Table 1; EIMS (probe) 70 eV, *m/z* (rel. int.): 424 $[M]^+$ (46), 409 (100), 381 (17), 379 (10), 369 $[M - C_4H_7]^+$ (14), 355 (4), 212 (2), 197 (4), 177 (10).

Xanthone V_{1a} [1,5,6-*trihydroxy*-2,4-*di*(3,3-*dimethylprop*-2-*enyl*) *xanthone*] (**4**). Brown solid (Et_2O hexane), mp 176 179°. UV λ_{max}^{MeOH} nm (log ε): 253, 330 (4.14, 3.91); λ_{max}^{NaOAc} 261, 372; $\lambda_{max}^{NaOAc + H_3BO_3}$ 263, 351, 371 sh; $\lambda_{max}^{AlCl_3}$ 278, 401; $\lambda_{max}^{AlCl_3 + HCl}$ 257, 273, 349; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3410, 1620, 1585; ^1H NMR (60 MHz, Me_2CO-d_6): δ13.42 (1H, *s*, OH-1), 7.80 (1H, *d*, J = 8 Hz, H-8), 6.93 (1H, *d*, J = 8 Hz, H-7), 5.40–5.05 (2H, *m*), 3.65 (2H, *d*, J = 7 Hz), 3.45 (2H, *d*, J = 7 Hz), 1.86 (3H, *s*), 1.77 (3H, *s*), 1.68 (6H, *s*); EIMS (probe) 70 eV, *m/z* (rel. int.): 396 $[M]^+$ (88), 341 $[M - C_4H_7]^+$ (42), 325 (65), 311 (4), 297 (51), 285 $[341 - C_4H_8]^+$ (100); m* 293.6 (396 → 341) and 238.2 (341 → 285).

Xanthone V_{2a} [1,5,6-*trihydroxy*-7-*methoxy*-2,4-*di*(3,3-*dimethylprop*-2-*enyl*) *xanthone*] (**5**). Brown solid (Et_2O hexane), mp 170–173°. UV λ_{max}^{MeOH} nm (log ε): 267, 283 sh, 332 (3.82, 3.78, 3.57); λ_{max}^{NaOAc} 267, 385; $\lambda_{max}^{NaOAc + H_3BO_3}$ 267, 359; $\lambda_{max}^{AlCl_3}$ 280, 373 (403 after 20 min); $\lambda_{max}^{AlCl_3 + HCl}$ 278, 361, 420 sh; IR ν_{max}^{KBr} cm^{-1}: 3400, 1640–1600; ^1H NMR (60 MHz, Me_2CO-d_6): δ13.40 (1H, *s*, OH-1), 7.15 (1H, *s*, H-8), 5.45–5.0 (2H, *m*), 3.90 (3H, *s*), 3.62 (2H, *d*, J = 7 Hz), 3.38 (2H, *d*, J = 7 Hz), 1.87 (3H, *s*), 1.78 (3H, *s*), 1.66 (6H, *s*); EIMS (probe) 70 eV, *m/z* (rel. int.): 426 $[M]^+$ (90), 371 $[M - C_4H_7]^+$ (50), 355 (70), 341 (18), 327 (62), 315 $[371 - C_4H_8]^+$ (100).

Acknowledgements –The work was supported by a grant from Progetto Finalizzato Chimica Fine e Secondaria, C.N.R. We thank Dr. M. Nicolai, Dipartimento di Chimica, Università La Sapienza, Roma, for mass spectra.

REFERENCES

1. Moura Pinheiro, R., Marquina Mac-Quhae, M., Marini Bettolo, G. B. and Delle Monache, F. (1984) *Phytochemistry* **23**, 1737.
2. Delle Monache, F. (1985) *Rev. Latinoam. Quim.* **16**, 5.
3. Hutchinson, J. and Dalziel, J. M. (1954) *Flora of West Tropical Africa* (revised by Keay, R. W.) 2nd edn, Vol. 1 (part 1), p. 288. Whitefriars, London.
4. *Index Kewensis* (1895) 1212; suppl. IV (1906–10) and VI (1931).
5. Kerharo, J. O. (1974) *La Pharmacopée sénégalaise traditionelle*, p. 485. Vigot Freres, Paris.
6. Mathis, C. and Ourisson, G. (1964) *Phytochemistry* **3**, 133.
7. Botta, B., Delle Monache, F., Delle Monache, G., Marini Bettolo, G. B. and Msonthi, J. D. (1985) *Phytochemistry* **24**, 827.
8. Botta, B., Delle Monache, F., Delle Monache, G., Marini Bettolo, G. B. and Oguakwa, J. U. (1983) *Phytochemistry* **22**, 539.
9. Delle Monache, F., Botta, B., Nicoletti, M., de Barros Côelho, J. S. and de Andrade Lyra, F. D. (1981) *J. Chem. Soc. Perkin Trans.* 1, 484.
10. Barraclough, D., Locksley, H. D., Scheinmann, F., Taveira Magalhaes, M. and Gottlieb, O. R. (1970) *J. Chem. Soc.* (*B*) 603.
11. Nakano, T., Alonso, J., Grillet, R. and Martin, A. (1979) *J. Chem. Soc. Perkin Trans.* 1, 2107.
12. Delle Monache, F., Marquina Mac-Quhae, M., Marini Bettolo, G. B. and Alves de Lima, R. (1983) *Phytochemistry* **22**, 227.