1,2,3-*Trimethoxy*-5-(1-*propenyl*) *benzene*; trans-*iso*-*elemicin*) **3**. The IR spectra were superimposable with that reported in ref. [10]. Additional spectroscopic data were obtained from the 80 MHz FT-^{1}H NMR spectra ($CDCl_3$) which showed: δ 6.52 (2 H, *s*); ABX_3 system 6.31 (1 H, *d*, *br*), 6.1 (1 H, *dq*, J_{AB} = 16 Hz), 1.87 (*d*, *br*, J_{BX} = 6 Hz), 3.87 (6 H, *s*), 3.82 (3 H, *s*). MS: *m/e* 208 (M^+, 100), 193 (M^+ − Me, 85.5), 177 (M^+ − Me, 5.8), 165 (M^+ − C_2H_3O, 12.3).

1,2,3,4-*Tetramethoxy*-5-(1-*propenyl*) *benzene*; (trans-*isomyristicin*) **4**. The 90 MHz ^{1}H NMR spectrum ($CDCl_3$) shows: δ 6.81 (1 H, *s*), ABX_3 system 6.49 (1 H, *d*, *br*), 6.23 (1 H, *dq*, J_{AB} = 16.5 Hz), 1.90 (*d*, *br*, J_{BX} = 6 Hz); 3.96 (3 H, *s*), 3.93 (3 H, *s*), 3.90 (3 H, *s*) and 3.83 (3 H, *s*). MS: *m/e* 238 (M^+, 100), 223 (M^+ − Me, 22), 195 (M^+ − Me + CO, 17.2), 192 (M^+ − Me + OMe, 63.4).

The chemical shifts of the aromatic protons of **3** and **4** correlated with the corresponding values of the tri- and tetra-methoxybenzenes reported in the literature [14]. In the case of **3**, the chemical shifts of δ 6.44 and 5.91 respectively were used for comparison with the experimental value of 6.52 found with the propenyl derivative. Considering that the type of double bond involved will generally cause a downfield effect on the protons in the *ortho* position, **3** can be directly correlated with a 1,2,3-methoxyl substitution. In a similar manner, those chemical shifts in the two 1,2,3,4- and 1,2,3,5-tetramethoxybenzenes (δ 6.42 and 5.95, respectively) excluded the latter when these were compared to the experimental value of 6.81 found for **4**.

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PRENYLATED BENZOPHENONES FROM *VISMIA DECIPIENS*

G. DELLE MONACHE, J. GONZALEZ GONZALEZ†, F. DELLE MONACHE and G. B. MARINI BETTOLO‡

Centro Chimica dei Recettori del C.N.R., Università Cattolica del S. Cuore, Via della Pineta Sacchetti, 644–00168 Rome, Italy

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Key Word Index—*Vismia decipiens*; Guttiferae; vismiaphenone A and B; *iso*-vismiaphenone B; physcion.

INTRODUCTION

During the systematic study [1–5] of the components of the South American species of *Vismia* (Guttiferae), we isolated from the fruits the known harunganin [6] and nine new prenylated anthranoids (i.e. vismione A and B, deacetylvismione A, ferruginin A and B, vismin, ferruanthrone, γ-hydroxyferruginin A and γ,γ'-dihydroxy-ferruginin A). In the fruits of *V. decipiens*, collected in Brazil, besides ferruginin A, γ-hydroxy- and γ,γ'-dihydroxy-ferruginin A, three other less polar pigments are present [5]. This paper deals with the structural determination of these pigments, which were named vismiaphenone A and B and *iso*-vismiaphenone B.

RESULTS AND DISCUSSION

Vismiaphenone A, $C_{24}H_{28}O_4$ (M^+ 380), showed IR (ν_{CO} at 1600 cm^{-1}), UV (Table 1) and MS (ion at *m/e* 105) suggesting the structure of a benzophenone with one unsubstituted ring. The bathochromic shifts of the UV maxima (Table 1) after addition of $AlCl_3$ (+34 nm) and of

* Part VI in the series "Chemistry of the *Vismia* Genus". For Part V see ref. [5].

† Fellowship of IILA-CNR.

‡ To whom correspondence should be addressed.

Table 1. UV spectra (λ_{max}, nm) of vismiaphenones and derivatives

	MeOH	+NaOAc	+$AlCl_3$* (after 15 min)
Vismiaphenone A (**1**)	256, 310	256 *sh*, 315 *sh*, 365	256 *sh*, 310 *sh*, 344
Dichromane (**2**)	249, 300 *sh*	†	†
Chromene (**3**)	273, 323	†	273, 343
Dichromene (**4**)	255, 274 *sh*	†	†
Vismiaphenone B (**5**)	281, 319	282, 317	281, 348
Chromene (**6**)	258, 313 *sh*	†	244, 285 *sh*, 345
Chromene (**7**)	253, 284 *sh*	†	†
Iso-vismiaphenone B (**8**)	295, 305	295, 353	295, 339

* The spectra were recorded after 15–20 min because, in the presence of a bulky substituent in the *ortho* position to the chelated hydroxyl, the shift is not immediate [7].

† Unchanged.

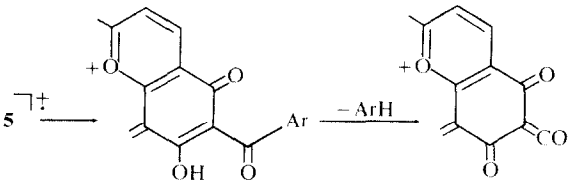
NaOAc (+55 nm), indicated that in the second ring two of the substituents were hydroxyls in *ortho* and *para* positions respectively to the carbonyl function. The presence of these two hydroxyls was confirmed by the ^{1}H NMR spectrum (Table 2), which exhibited a sharp singlet at δ 11.73 and a broad one at 6.25, both disappearing after addition of D_2O. Signals due to the other substituents (a methoxyl and two γ,γ-dimethylallyl chains) were also evident. The ^{1}H NMR spectrum was completed by a complex multiplet (5H) between 7.80 and 7.30, which was attributed to the unsubstituted aromatic ring. In pyridine-d_5 the signals of the two methylene protons were shifted (Table 2) to low field (0.45 and 0.32 ppm, respectively), suggesting that the prenyl groups must be adjacent to phenolic hydroxyl groups [3, 7].

On the basis of these findings, structure **1** was assigned to vismiaphenone A. The low chemical shift value of the C-6 methoxyl can be explained by the shielding effect of the unsubstituted aromatic ring, as previously observed [8] for 2-hydroxy-6-methoxybenzophenones. Acid-catalysed cyclization gave the dichromane **2**, while cyclodehydrogenation with DDQ (2,6-dichloro-3,5-dicyanbenzoquinone) yielded the chromenes **3** and **4**, thus confirming the proposed structure for vismiaphenone A. Also vismiaphenone B, $C_{23}H_{24}O_4$ (M^+ *m/e* 364), showed spectral features (Tables 1 and 2 and Experimental) consistent with the structure of a benzophenone having the first ring unsubstituted, but lacking *para*-hydroxyl on the latter. The presence of a γ,γ-dimethylallyl chain and a 2,2-dimethylchromene ring was evidenced by the ^{1}H NMR spectrum (Table 2), while methoxy-groups were absent.

The low-field shifts (Table 2) in pyridine-d_5 of the CH_2 (0.40 ppm) and of the CH_α (0.35 ppm) suggested again that both the substituents were adjacent to phenolic hydroxyl groups [3, 7]. Two broad singlets, labile with D_2O, at δ 9.20 and 8.78 ($CDCl_3$) were present; the chemical shift value was apparently low for a chelated hydroxyl but it was analogous to those values observed for other 2,6-dihydroxybenzophenones [9, 10]. Consequently structure **5** was assigned to vismiaphenone B. To confirm this structure, vismiaphenone B was correlated to vismiaphenone A by methylation with CH_2N_2, which led to the formation of a mono- and a dimethyl derivative. Dimethyl-vismiaphenone B was identical to the methyl derivative **7** obtained from the chromene **3**. On the basis of the spectral evidence for monomethyl-vismiaphenone B, which was not identical to chromene **3**, the isomeric structure **6** was assigned.

Iso-vismiaphenone B, $C_{23}H_{24}O_4$ (M^+ *m/e* 364) presented the same substitution pattern of vismiaphenone B. In the ^{1}H NMR spectrum (Table 2) only one chelated hydroxyl (sharp singlet at δ 12.80) was present.

A second phenolic hydroxyl group was located on C-4 because of the bathochromic shift in the UV spectrum after addition of NaOAc (Table 1). Consequently structure **8** was assigned to *iso*-vismaphenone B. Notably, in the MS of these benzophenones, after the typical loss of one or both the substituents, a molecule of benzene (unsubstituted ring plus 1H) was lost. A formal example of this loss for vismiaphenone B is given in Scheme 1.



Scheme 1.

Benzophenones are quite rare natural products [8]. Marupone [11] is the only true example of a prenylated benzophenone previously reported in Guttiferae, whereas bronianone [12] and xanthochymol [13] have a modified B ring.

Vismiaphenone A and B and *iso*-vismiaphenone B represent a further example of prenylated compounds in the genus *Vismia* and their co-occurrence with prenylated anthranoids [5] may be of taxonomic value.

EXPERIMENTAL

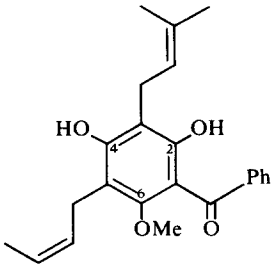
Plant material. The berries of *Vismia decipiens* Schlecht-Cham., syn. *V. pentagina* (Spreng) Ewan, comb. nov., were collected in November 1978 near Brasilia (Reserva do Instituto Brasileiro de Geografia e Estatistica) and identified by Dr. J. E. De Paula (Universidade Federal de Brasilia). A voucher sample is in the Herbarium of CCR under the cipher RAL N. 2.

Extraction and separation. The berries (350 g) were extracted with $CHCl_3$ to give a dark orange viscous oil (25 g) after removal of the solvent. The crude extract was chromatographed on Si gel and the column was eluted with $CHCl_3$ to give a mixture of benzophenones and triglycerides (fraction A), and triglycerides (6.8 g). Further elution with $CHCl_3$–MeOH (95:5) gave succesively [5] ferruginin A, fatty acids, γ-hydroxyferruginin A and γ,γ'-dihydroxyferruginin A. Extended chromatographic purification of fraction A (6.8 g) with C_nH_n gave vismiaphenone A

Table 2. ^{1}H NMR spectral data of the benzophenones from *V. decipiens**

	Ph– (5 H, *m*)	C-2 (1 H, *s*)	C-3	C-4 (1 H, *br s*)	C-5	C-6 (*s*)
Vismiaphenone A (**1**)	7.80–7.30	11.70	3.40†, ‖ 5.25‡ ~1.75 (6 H)	6.25	3.28†, ¶ 5.18‡ ~1.75 (6 H)	3.18 (3 H)
Vismiaphenone B (**5**)	7.70–7.35	9.20	6.57§, †† 5.45§ 1.41 (6 H)	—	3.22†, ** 5.15‡ 1.75 (3 H) 1.67 (3 H)	8.78
Iso-vismiaphenone B (**8**)	7.60–7.30	12.80	3.41† 5.25‡ ~1.77 (6 H)	6.30	6.50§ 5.23§ 0.97 (6 H)	—

* δ values in $CDCl_3$ (60 MHz). $\Delta\delta = \delta_{C_5D_5N} - \delta_{CDCl_3}$.
† 2 H, *br d*, J = 7 HZ.
‡ 1 H, *br t*, J = 7 Hz.
§ 1 H, *d*, J = 10 Hz.
‖ $\Delta\delta$ = +0.45.
¶ $\Delta\delta$ = +0.32.
** $\Delta\delta$ = +0.40.
†† $\Delta\delta$ = +0.36.



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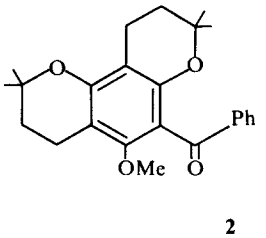
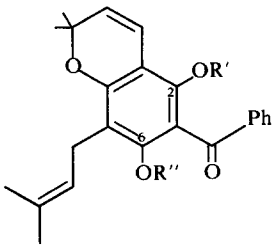
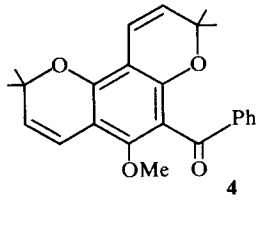


2

DDQ



	R′	R″
3	H	Me
5	H	H
6	Me	H
7	Me	Me



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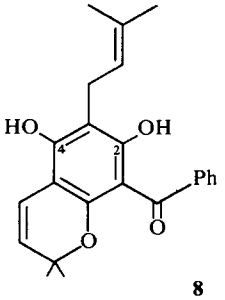

8

(500 mg), *iso*-vismiaphenone B (110 mg), vismiaphenone B (600 mg) and physcion (150 mg).

Vismiaphenone A (**1**). Oil (Found: C, 75.92; H, 7.20. $C_{24}H_{28}O_4$ requires: C, 75.76; H, 7.41 %). UV in Table 1. ^{1}H NMR in Table 2. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1615 (*sh*), 1602, 1580 (*sh*), 1442, 1375, 1320, 1285, 1175, 1092. MS, *m/e* (rel. int.): 380 (M^+, 100), 365 (M − 15, 34), 363 (M − 17, 44), 325 (M − 55, 44), 324 (M − 56, 20), 310 (M − 70, 96), 309 (20), 307 (16), 269 (325 − 56, 47), 233 (310 − 77, 20), 231 (16), 191 (269 − 78, 18), 105 (Ph—C≡O$^+$, 40), 77 (5): m* 350.6 (380 → 365), m* 340.8 (380 → 363).

Cyclization of vismiaphenone A. Vismiaphenone A (50 mg) in $CHCl_3$ (5 ml) and TFA (0.5 ml) was left to stand overnight. Evapn and chromatographic purification (Si, C_6H_6) afforded dicyclovismiaphenone A **2** (30 mg); white needles, mp 145–146° (heptane). UV in Table 1. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660, 1595. ^{1}H NMR ($CDCl_3$): δ 7.85 – 7.65 (2 H, *m*), 7.45 – 7.25 (3 H, *m*), 3.63 (3 H, *s*), 2.68 (2 H, *t*, J = 7 Hz), 2.57 (2 H, *t*, J = 7 Hz), 1.77 (2 H, *t*, J = 7 Hz), 1.64 (2 H, *t*, J = 7 Hz), 1.32 (6 H, *s*), MS, *m/e* (rel. int.): 380 (M^+, 100), 365 (M − 15, 9), 363 (8), 325 (M − 55, 94), 324 (M − 56, 48), 309 (18), 307 (5), 303 (M − 77, 4), 269 (325 − 56, 39), 247 (4), 191 (269 − 78, 26), 105 (Ph—C≡O$^+$, 29), 77 (23): m* 350.6 (380 → 365), m* 277.3 (380 → 325), m* 276.3 (380 → 324) m* 135, 6 (269 → 191).

Cyclodehydrogenation of vismiaphenone A. Vismiaphenone A (50 mg) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 30 mg) in C_6H_6 were refluxed for 1 hr. After filtration of DDQ–H_2, evapn and chromatographic separation (Si, C_6H_6) 20 mg of chromene I (**3**) and 15 mg of dichromene II (**4**) were obtained. Chromene I (**3**); UV in Table 1. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3380, 1640, 1580, 882, ^{1}H NMR ($CDCl_3$): δ 11.78 (1 H, *s*), 7.75 – 7.30 (5 H, *m*), 6.68 (1 H, *d*, J = 9 Hz), 5.50 (1 H, *d*, J = 9 Hz), 5.15 (1 H, *br t*, J = 7 Hz), 3.40 (2 H, *br d*, J = 7 Hz), 3.18 (3 H, *s*), 1.75 (6 H, *br s*), 1.46 (6 H, *s*): $\Delta\delta = \delta$ (C_5D_5N) − δ($CDCl_3$) + 0.26 (CH_α), +0.08 (CH_2). Dichromene II (**4**); UV in Table 1. IR ($CHCl_3$) $\nu_{max}^{CHCl_3}$ cm^{-1}: 1665, 1642, 1600, 1585, 880. ^{1}H NMR ($CDCl_3$): δ 7.90 – 7.75 (2 H, *m*), 7.50 – 7.30 (3 H, *m*), 6.58 (1 H, *d*, J = 10 Hz), 6.48 (1 H, *d*, J = 10 Hz), 5.50 (1 H, *d*, J = 10 Hz),

5.33 (1 H, *d*, $J = 10$ Hz), 3.65 (3 H, *s*), 1.45 (6 H, *s*), 1.17 (6 H, *s*). Chromene I (**3**) with CH_2N_2 gave dimethyl-vismiaphenone B, **7** (TLC, ^{1}H NMR, IR).

Vismiaphenone B (**5**). Oil (Found: C, 76.05; H, 6.50. $C_{23}H_{24}O_4$ requires: C, 75.80; H, 6.64%). UV in Table 1. ^{1}H NMR in Table 2. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3350, 3390, 1642 sh, 1615, 1592 (sh), 1570, 1175, 1128, 880. MS, *m/e* (rel. int.): 364 (M^+, 66), 349 (M − 15, 100), 309 (M − 55, 57), 293 (349 − 56, 53), 281 (12), 231 (309 − 78, 9), 215 (293 − 78, 10), 105 (Ph−C≡O$^+$, 45), 77 (5): m* 246 (349 → 293).

Methylation with CH_2N_2 yielded a mono- and di-methyl derivatives after chromatographic separation (Si, C_6H_{12}–C_6H_6, 1:1). *Monomethyl-vismiaphenone B* (**6**): oil; UV in Table 1. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1640, 1605, 1582, 880. ^{1}H NMR ($CDCl_3$): δ 12.10 (1 H, *s*), 7.75–7.30 (5 H, *m*), 6.42 (1 H, *d*, $J = 10$ Hz), 5.52 (1 H, *d*, $J = 10$ Hz), 5.15 (1 H, *br t*, $J = 7$ Hz), 3.33 (2 H, *br d*, $J = 7$ Hz), 3.15 (3 H, *s*), 1.81 (3 H, *s*), 1.72 (3 *H*, *s*), 1.44 (6 H, *s*), $\Delta\delta = \delta$ (C_5D_5N) − δ ($CDCl_3$) + 0.14 (CH_3) + 0.31 (CH_2).

Dimethyl-vismiaphenone B (**7**). Oil: UV in Table 1. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1665, 1600, 1590, 880. ^{1}H NMR ($CDCl_3$): δ 7.90–7.70 (2 H, *m*), 7.55–7.30 (3 H, *m*), 6.56 (1 H, *d*, $J = 10$ Hz), 5.55 (1 H, *d*, $J = 10$ Hz), 5.15 (1 H, *br t*, $J = 7$ Hz), 3.58 (3 H, *s*), 3.55 (3 H, *s*), 3.26 (2 H, *d*, $J = 7$ Hz), 1.73 (3 H, *s*), 1.67 (3 H, *s*), 1.33 (6 H, *s*).

Iso-*vismiaphenone B* (**8**). Yellow micro-crystals, mp 118–120° (heptane). [Found: C, 75.92; H 6.55. $C_{23}H_{24}O_4$ requires: C, 75.80, H 6.64%]. UV in Table 1. ^{1}H NMR in Table 2. MS, *m/e* (rel. int.): 364 (M^+, 47), 349 (M − 15, 82), 321 (12) 309 (M − 55, 22), 293 (349 − 56, 100), 231 (7), 215 (293 − 78, 48), 105 (Ph−C=O$^+$, 77), 77 (66); m* 334.6 (364 → 349), m* 246 (349 → 293), 157.8 (293 → 215).

Physcion. Identified by comparison with an authentic sample (mmp., TLC, ^{1}H NMR).

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