Tetrahedron Vol. 35, pp. 2143 to 2149

0040-4020/79/0915-2143/$02.00/0

FERRUGININ A AND B AND FERRUANTHRONE, NEW TRIPRENYLATED ANTHRANOIDS FROM *VISMIA BACCIFERA VAR. FERRUGINEA*

F. DELLE MONACHE, M. MARQUINA MC QUHAE, F. FERRARI and G. B. MARINI-BETTOLO*

C.N.R., Centro Chimica dei Recettori e delle Molecole Biologicamente Attive, presso Università Cattolica; Via Pineta Sacchetti, 644, 00168 Roma, Italy

(*Received in UK 12 February 1979*)

Abstract—The isolation of the new triprenylated anthranoids—ferruginin A and B and ferruanthrone—and the known harunganin is reported. The structure of the ferruginins was established by chemical and spectroscopical methods and by their thermal rearrangement to anthrones.

On the basis of the PMR spectra in C_5D_5N of the rearrangement products and of ferruanthrone, a revised structure of harongin anthrone is proposed.

In previous papers we reported the isolation and identification of the sesquiterpenes,[1] as well as the structure determination of the two new pigments,[2] vismione A 1 and B 2, isolated from the berries of *Vismia baccifera* var. *dealbata* (Guttiferae).

In view of the interest in the particular structures of the pigments, we have examined other *Vismia* sp. and the present paper is concerned with the constituents of *Vismia baccifera* var. *ferruginea*, collected near Caracas (Venezuela).

By conventional procedures we isolated from the chloroform extract of the berries four isomeric pigments ($C_{30}H_{36}O_4$), which were denominated ferruginins A, B and C and ferruanthrone, as well as a small quantity of vismione B, vismione A and its artefacts.[2]

The IR spectra of ferruginins showed H- bonded CO bands and their UV visible spectra provided evidence of a common feature for each of the compounds (Table 1). These data show a close similarity to those of the vismiones, with some difference in the second band of the UV spectra.

The PMR spectrum in acetone-d_6 of the main component, ferruginin A, showed evidence of an aromatic Me group, three aromatic/olefinic protons, one γ-γ dimethylallyl side chain on an aromatic nucleus (δ 5.10, 1H, t, J 7 Hz; δ 3.47, 2H, d, J 7 Hz; δ 1.80, 3H, s; δ 1.67, 3H, s) and two phenolic OH groups, one of which was highly chelated (δ 10.35 and 17.75, ss). The presence of a third phenolic or enolic OH group, not evidenced in the PMR spectrum in acetone-d_6, was established by methylation with ethereal diazomethane, which gave *inter alia* a monomethyl derivative still containing two phenolic OH groups. The remaining PMR resonances in the spectrum of ferruginin A were a two proton triplet (δ 4.65, J 7 Hz), a four proton multiplet (centered at δ 2.86) and a twelve proton broad singlet (δ 1.43), which were attributed to two gem-di-C-prenyls, a fact in accordance with a predominant loss of 68 mu from the molecular ion in the mass spectrum.[3] The presence of three prenyl chains was confirmed by catalytic hydrogenation to give a hexahydro derivative (M^+ at *m/e* 466) with loss of 70 mu both from the molecular ion and from the base peak (*m/e* 409; M^+ −57 mu). The literature reports a substance, $C_{30}H_{36}O_4$, harunganin, isolated from *Harungana madagascariensis*, which shows spectroscopic characteristics similar to ferruginin A. By X-ray chrystallography Stout *et al.*[4] proved that it has the rather uncommon structure 3 and Richtie and Taylor reported[3b,5] chemical and spectroscopical studies.

Because a direct comparison between ferruginin A and

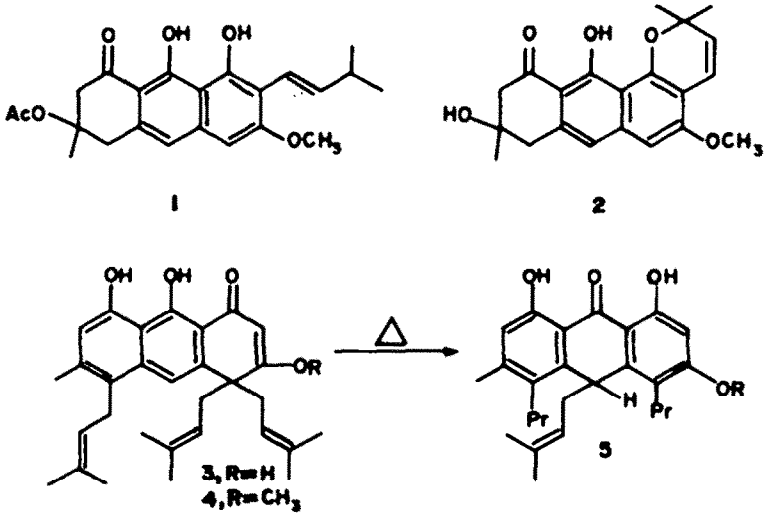


Table 1. UV-visible (EtOH) and IR spectra ($CHCl_3$) of anthranoids from *Vismia* sp

	λ max, nm	ν max, cm^{-1}
Ferruginin A, 9	243, 321, 412	3380, 1630, 1590-1570
Ferruginin B, 14	242, 321, 414	3350, 1630, 1600-1580
Ferruginin C	242, 323, 412	3350, 1630, 1600-1590
Vismione A, 1	243, 291, 410	3350, 1720, 1620-1600
Vismione B, 2	241, 278, 410	3400, 1610-1600
Ferruanthrone, 18	240, 256, 275, 313, 365	3370, 1610-1590

harunganin was not possible on the basis of differences of m.p. and solubility and in its behavior on methylation, it can be inferred that ferruginin A is an isomer of harunganin where the aromatic prenyl chain is in a different position.

The most interesting observation[5] on the chemistry of harunganin was the rearrangment of its 3-methylether, 4, to the anthrone 5 (R = Me) by brief heating at 180°. Similar treatment of ferruginin A afforded three isomeric products (M^+ at *m/e* 460), which were named anthrones A_1, A_2 and A_3 on the basis of their UV visible spectra (Experimental).

The PMR spectra ($CDCl_3$) of the anthrones A_1 and A_3 showed only one aromatic proton, three prenyls on the aromatic nucleus and the characteristic[6] singlet ($\delta \sim 4.0$) due to the methylene on C_{10}.

On the other hand the PMR spectrum of the anthrone A_2 displayed two aromatic protons, two prenyls on the aromatic nucleus and the sequence $\diagdown$CH-Pr, as established by decoupling experiments and confirmed by the loss of 68 mu from the molecular ion in the mass spectrum. As in the PMR spectrum[5] of the anthrone 5, the unusual chemical shifts of the allylic Me signals (δ 1.50 and 0.97) of the prenyl chain on C_{10} were observed.

These findings prove that ferruginin A rearranges by heating to anthrone, while one of the prenyl chain on C_4 shifts to one of the free positions.

The structures of the anthrones A_1, A_2 and A_3 were established as 6, 7 R = R_1 = H and 8 respectively by PMR spectra in pyridine-d_5 (see below); it follows that ferruginin A is 9 (R = R_1 = H).

Further confirmation of the structure of the anthrones A_3 and A_2 was obtained from their acetyl derivatives. While the anthrone A_3 gave a tetraacetyl derivative 10, having a typical anthracene UV spectrum, the anthrone A_2 yielded a diacetyl, 7, (R = Ac, R_1 = H) and a triacetyl derivative, 7 (R = R_1 = Ac), both maintaining an anthrone UV visible spectrum. Evidently as reported[7] for similar compounds, the presence of a chain at C_{10} prevents the equilibrium anthrone-anthrol. Final proof of the location on C_7 of the aromatic prenyl of ferruginin A was obtained through its acid catalyzed cyclisation to chromane. The anthrone A_2 gave with trifluoroacetic acid two products: the first one, 11 (M^+ at *m/e* 460), showed in the PMR spectrum one unaffected aliphatic prenyl chain and two chromane ring systems; the second, less polar product, 12 exhibited M^+ at *m/e* 476 (i.e. addition of one mole of water to the aliphatic prenyl chain) and two chromane ring systems in the PMR spectrum. Moreover *only one* chelated OH group was present in PMR spectra of both the anthrones 11 and 12; that means that one chromane ring is closed on the phenolic OH at C_8 (not at C_1 because ferruginin A had an unsubstituted C_2).

By the same treatment the anthrone A_3 yielded the anthraquinone 13, M^+ 492 (i.e. addition of one mole of water to a prenyl not adjacent to OH and oxidation to anthraquinone by atmospheric oxygen), also exhibiting a single chelated OH group in the PMR spectrum. The isomeric ferruginin B, $C_{30}H_{36}O_4$, (UV, visible and IR spectral data in Table 1) also displayed in the PMR spectrum two gem-di-C prenyl chains and one prenyl on an unsaturated carbon.

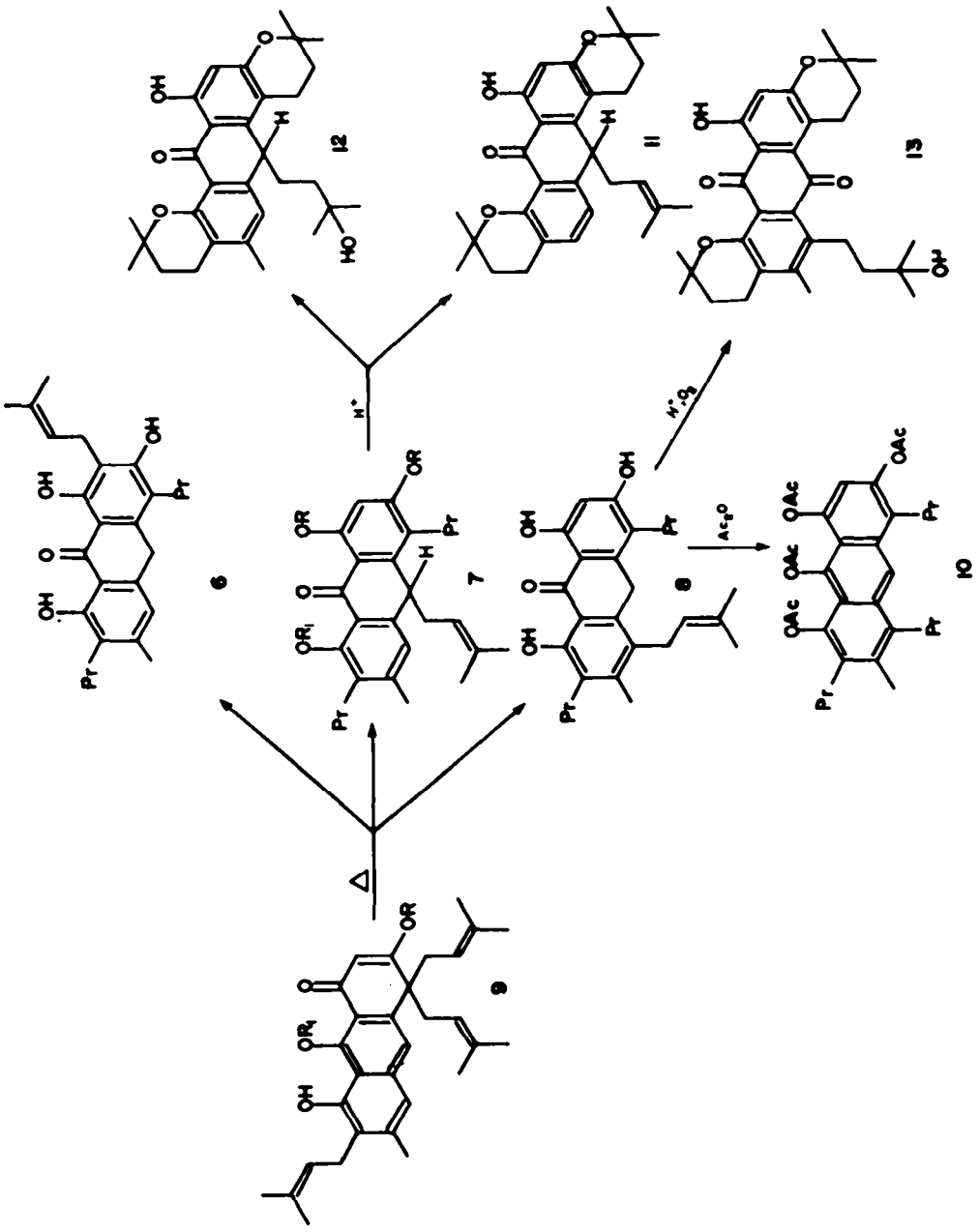
The signal due to the proton on the C_2 being absent in the PMR spectrum, we located the third phenyl chain in this position; thus to ferruginin B the structure 14 was assigned. Thermal rearrangement of ferruginin B afforded three products, which were indicated as anthrones B_1, B_2 and B_3.

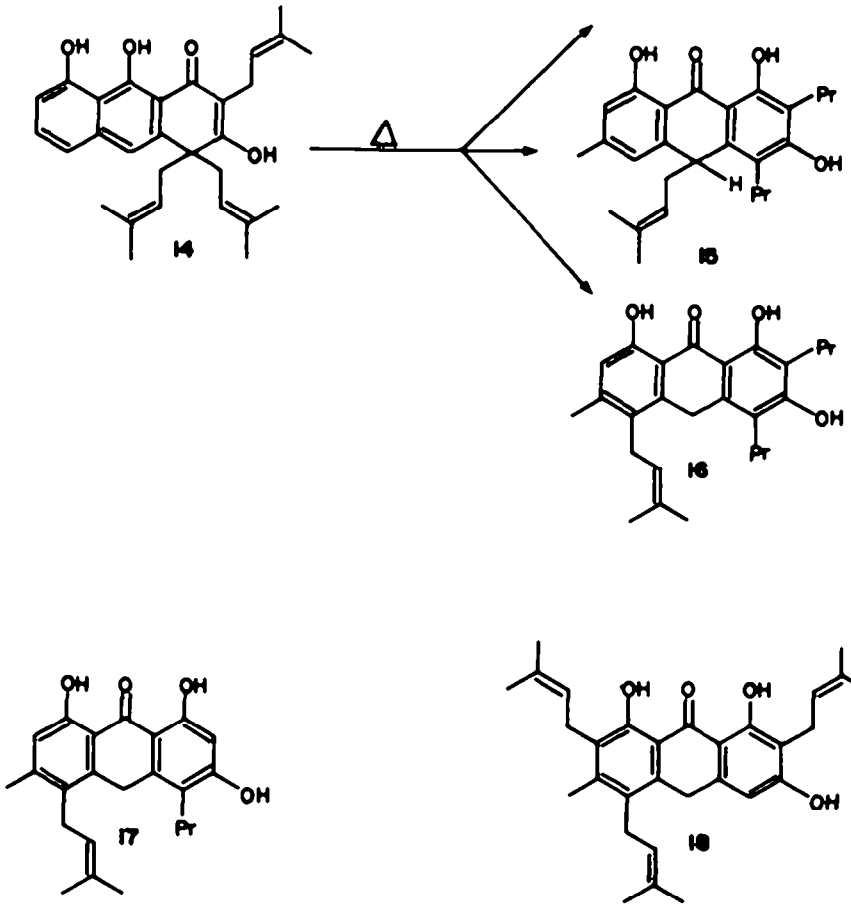
The anthrone B_1 proved identical to the anthrone A_1 (6). The anthrones B_2 and B_3 have been assigned the structures 15 and 16 respectively on the basis of the spectral data and particularly of the PMR spectra in pyridine $-d_5$ (see below).

The third isomer ferruginin C, $C_{30}H_{36}O_4$, m.p. 170-5°, also contained two aliphatic and one aromatic prenyl chains. Although it gave a single spot on tlc, the PMR spectrum evidenced that the sample was contaminated with a compound lacking the aromatic prenyl chain: this follows from the intensity of the aromatic prenyl signals with respect to those of the two aliphatic prenyls (ratio <1/2), from the presence of two series of aromatic protons and of an additional aromatic proton signal (δ 7.05, integrated for 0.3 proton). Two further crystallizations from acetone raised the m.p. to 185-8° and a pure compound was obtained. From the above data ferruginin C was identified with harunganin 3. Brief heating of ferruginin C, m.p. 170-5°, yielded four products, which were named anthrone HR_1, HR_2, HR_3 and HR_4.

The anthrones HR_1 and HR_3 proved to be identical to the anthrones B_3 (16) and A_3 (8) respectively. To the anthrone HR_2 the structure 5 (R = H) was assigned on the basis of the spectroscopic data. On the other hand to the anthrone HR_4 (M^+ at *m/e* 392 in the mass spectrum), showing *two* aromatic protons and *only two* prenyl chains, the structure 17 was attributed. The isolation of the anthrone 17 from the thermal rearrangement of the crude ferruginin C, was considered to be confirmation of the presence of an impurity without the aromatic prenyl chain.

Finally, ferruanthrone, $C_{30}H_{36}O_4$, was characterized as a triprenylated anthrone containing an aromatic Me and three phenolic OH groups (two of which chelated) from its UV visible and PMR spectra. Formation of a tetraacetyl derivative with light absorption properties





typical of an anthracene and the presence in the PMR spectrum of a signal (δ 3.90, 2H) corresponding to the C_{10}-methylene, suggest that ferruanthrone is an isomer of the anthrones A_1, A_3 and B_3, from which it differs in both m.p. and chromatographic behavior. Consequently the only possible structure of the ferruanthrone is **18**.

A study of the PMR spectra in pyridine–d_5 of the four isomeric triprenylated anthrones A_1, A_3, B_3 and ferruanthrone supported the assigned structures. It is known[8] that the aromatic solvents cause large shifts of the PMR signals and in the case of phenolic compounds in pyridine this was attributed[9] to the formation of a collision complex between the phenolic OH and the nitrogen of the solvent. Recently this method was elaborated[10] for the study of prenylated phenols and the different behavior of the benzylic methylene of the prenyl, according to its closeness to two, one or no OH group, was evidenced.

Table 2 shows the chemical shifts in pyridine–d_5 of the prenyls and of the aromatic proton of the four isomeric triprenylated anthrones A_1, A_3, B_3 and ferruanthrone. The above data indicate that it is possible to distinguish by this method a prenyl on C_2 (between two OH groups), from one on C_4 or C_7 (adjacent to only one OH group) and from one on C_5 (without adjacent OH group). Indeed one C_2-prenyl gives in the PMR spectrum signals at $\delta \sim 3.84$ (benzylic methylene, d, J 7 Hz) and at $\delta \sim 5.65$ (unsaturated proton, t, J 7 Hz); one C_4–prenyl gives the same signals at $\delta \sim 3.67$ and $\delta \sim 5.30$, while one such group on C_5 signals at $\delta \sim 3.35$ and $\delta \sim 5.0$. Further support for the structures of the four isomeric anthrones was obtained from the values of $\Delta\delta = \delta_{C_5D_5N} - \delta_{CDCl_3}$, because a value of $\Delta\delta = +0.53$ for the C_2–H, of $\Delta\delta = +0.30$ for the C_4– or C_7–H, and of $\Delta\delta = +0.07$ for the C_5–H, can be calculated. It is noteworthy that the anthrones B_3 and ferruanthrone give practically the same PMR spectra (chemical shifts and fingerprint) both in pyridine–d_5 and in chloroform–d, and they can be differentiated only by the color, the R_f values and mixed m.p. Also the values for the diprenylated anthrone H_4 are in perfect agreement (Table 2), while those of the C_{10}-substituted anthrones A_2, B_2 and HR_2 show some discrepancies, particularly for the C_4– and C_7–substituent, which do not give the same values. It can be underlined that structure **16** was previously[3b] assigned, as the most likely, to harongin anthrone, m.p. 208°. Unfortunately a direct comparison was not possible, but it is our opinion that, having now available all four isomers, the correct structure of harongin anthrone should be **8** (anthrone A_3) on the basis of the following considerations: (1) the anthrone A_3 has m.p. very near to that reported[4] for harongin anthrone; (2) the m.p. 127–30° of the anthracene tetraacetyl derivative **10** of the anthrone A_3 is almost the same as reported[4] for the corresponding derivative (m.p. 130°) of harongin anthrone; (3) the chemical shifts (δ 6.33) reported[4] for the aromatic proton of harongin anthrone, even in a different solvent, seems to us more correctly attributable to a C_2–H (between two OH groups) than to a C_7–H. The finding of poly-prenylated derivatives in *Vismia* genus is a common feature of the secondary metabolism of all the plants of the family of Guttiferae.[11] The vismiones and

Table 2. Chemical shift (C_5D_5N) of the prenyls and $\Delta\delta$ of the aromatic protons

	C_2	C_6	C_7	C_8
Anthrone B_3 16	5.67 (1H) 3.83 (2H) 1.76 (6H)	5.27 (1H) 3.70 (2H) 1.76 (6H)	6.95 $\Delta\delta$ 0.32	5.00 (1H) 3.30 (2H) 1.76 (6H)
Anthrone A_3 8	6.82 $\Delta\delta$ [a] 0.55	5.35 (1H) 3.67 (2H) 1.70 (6H)	5.35 (1H) 3.67 (2H) 1.70 (6H)	5.05 (1H) 3.40 (2H) 1.70 (6H)
Ferruanthrone 18	5.63 (1H) 3.85 (2H) 1.75 (6H)	6.91 $\Delta\delta$ 0.31	5.25 (1H) 3.71 (2H) 1.75 (6H)	5.00 (1H) 3.32 (2H) 1.75 (6H)
Anthrone A_1 6	5.65 (1H) 3.84 (2H) 1.75 (6H)	5.30 (1H) 3.68 (2H) 1.74 (6H)	5.30 (1H) 3.68 (2H) 1.74 (6H)	6.70 $\Delta\delta$ 0.07
Anthrone HR_4 17	6.80 $\Delta\delta$ [a] 0.50	5.30 (1H) 3.65 (2H) 1.80 (6H)	6.92 $\Delta\delta$ [a] 0.26	5.00 (1H) 3.35 (2H) 1.80 (6H)
Anthrone HR_2 5, R = H	6.76 $\Delta\delta$ 0.46	5.47 (1H) 3.77 (2H) 1.86 (6H)	6.93 $\Delta\delta$ 0.27	5.10 (1H) 3.53 (2H) 1.77 (6H)
Anthrone A_2 7, $R=R_1=H$	6.73 $\Delta\delta$ 0.47	5.53 (1H) 3.70 (2H) 1.86 (6H)	5.27 (1H) 3.50 (2H) 1.70 (6H)	6.73 $\Delta\delta$ 0.19
Anthrone B_2 15	5.56 (1H) 3.83 (2H) 1.72 (6H)	5.47 (1H) 3.83 (2H) 1.72 (6H)	6.83 $\Delta\delta$ 0.23	6.70 $\Delta\delta$ 0.10

[a] Calculated from the spectrum in $CDCl_3$-CD_3OD, instead of $CDCl_3$.

ferruginins are tetrahydroanthracenes possessing new structures, although closely related to the anthrones, anthranols and antraquinones.

In order to have a better understanding of the relationship between natural anthracene derivatives in different oxidation states (tetrahydroanthranols, anthranols, anthrones, anthraquinones) present in many plant families, we propose for these group, in analogy with flavonoids, the comprehensive name of anthranoids. The occurence and the distribution in various species of these particular substances may be of some interest for the chemotaxonomy of *Vismia* genus, being the sole morphological approach insufficient to discriminate among the various species and varieties of this complicate genus.[12]

EXPERIMENTAL

UV spectra were recorded on a Beckmann Acta III, IR spectra on a Perkin–Elmer 247, mass spectra on an AEI 12, and PMR on a Varian EM 360 spectrometers (TMS as internal standard; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet). SiO_2 MN Kieselgel was for column chromatography and Kieselgel 60 F_{254} for tlc. M.ps are uncorrected.

Plant material. The berries of *Vismia baccifera var. ferruginea* (H.B.K.) were collected on February 1976 near Caracas (Venezuela) and identified in Instituto Venezolano de Investigaciones Cientificas. A voucher sample is in the Herbarium of Centro Chimica dei Recettori under the cipher VBF.

Extraction and separation. The berries (2 kg) were extracted with $CHCl_3$ to give a dark orange grease after removal of the solvent reduced under pressure. The crude extract was dissolved in hot petrol ether and the insoluble material was discarded by filtration. The filtrate was concentrated to a small volume and left standing overnight at −20°. Orange crystals (2.3 g) were separated by filtration and the mother liquors evaporated (20 g). The crystals gave two spots on tlc, which were separated on a silica-gel column eluted with $CHCl_3$ to give ferruginin A (1.4 g) and crude ferruginin C (0.8 g). The mother liquors were purified on a silica-gel column eluting with $CHCl_3$ containing increasing quantities of MeOH. The fractions were collected as shown in Table 3. The fractions I, II, IV and V were again chromatographed giving for each compound the quantities reported in the last column in Table 3.

Ferruginin A, 9 (R=R_1=H). Yellow crystals from CH_2Cl_2–heptane, m.p. 168–70°. (Found: (Calc. for $C_{30}H_{36}O_4$): C, 78.32 (78.23); H, 7.75 (7.88%) UV (EtOH) and IR spectra in Table 1. UV ($CHCl_3$), λ_{max}: 245, 267 sh, 280 sh, 320 sh, 420 nm (log ϵ: 4.49; 4.39, 4.32, 3.93, 4.02). PMR (acetone-d_6), δ: 17.75 (1H, s), 10.35 (1H, s), 7.26 (H_{10}, s), 7.02 (H_5, s, long range coupling with C_6-CH_3), 5.77 (H_2, s), 5.1 (1H, t, J 7 Hz), 4.65 (2H, t, J 7 HZ), 3.47 (2H, d, J 7 Hz), 2.86 (4H, heptet), 2.4 (3H, s), 1.8 (3H, s), 1.67 (3H, s), 1.43 (12 H, broad s). M/S, *m/e* (%): 460 (M^+, 23), 417 (3), 404 (12), 392 (100), 391 (38), 361 (13), 349 (20), 348 (18), 336 (20), 335 (13), 323 (12), 305 (14), 293 (48), 281 (25), 280 (8), 69 (26).

Methylation of ferruginin A with CH_2N_2. To ferruginin A (210 mg) in CH_2Cl_2 was added an excess of CH_2N_2 in Et_2O. The mixture was left to stand overnight at room temp. and the solvent evaporated. The residue was passed through a silica gel column eluted with CH_2Cl_2. 3-methyl-ferruginin A (13 mg), 1,9-dimethyl-isoferruginin A (26 mg), and 3,9-dimethyl-ferruginin A (56 mg) were successively eluted together minor quantities of unidentified products. *3-Methyl-ferruginin A* (9, R = CH_3, R_1 = H), oil. UV (EtOH), λ_{max} 243, 283, 420 nm. PMR ($CDCl_3$), δ: 16.85 (1H, s), 10.10 (1H, s), 3.74 (3H, s). MS, *m/e* (%): 474 (M^+, 14), 419 (5), 406 (34), 405 (100), 375 (6), 363 (18), 362 (15), 350 (12), 349 (9), 342 (13), 337 (13), 326 (16), 319 (15), 307 (50), 301 (10), 298 (16), 295 (28), 294 (9). *1,9 Dimethyl-isoferruginin A*, oil. UV (EtOH), λ_{max}: 245, 303, 383 nm. PMR ($CDCl_3$), δ: 9.93 (1H, s), 3.91 (3H, s), 3.86 (3H, s). MS, *m/e* (%): 488 (M^+, 56), 420 (100), 419 (72), 405 (6), 391 (16), 365 (24), 363 (14), 341 (16), 321 (22), 301 (22), 287

Table 3. Chromatographic separation of the mother liquors of *V. baccifera* var. *ferruginea*

Fractions	Weights (gr)	Eluition (% MeOH)	Composition (TLC)	2nd purification (gr)
I	5.6	0.7	Sesquiterpenes	-
			Artefacts of Vismione A	0.65
II	1.8	0.7	Sesquiterpenes	-
			Ferruanthrone	0.40
			Ferruginin B	0.60
III	2.5	0.7	Triglycerides	
IV	0.6	1.0	Triglycerides	-
			Vismione A	0.30
V	5.4	1.0	Triglycerides	-
			Ferruginin A	2.60
			Ferruginin C	0.75
			Vismione B	0.20
VI	2.2	1.0	Fatty acids	
VII	0.5	5.0	Fatty acids	
			Unidentified pigment	

(64). 3,9 *Dimethyl-ferruginin A* (9, R = R_1 = CH_3), m.p. 93–5° (petrol ether). UV (EtOH), λ_{max} 241, 269, 389 nm. PMR ($CDCl_3$), δ: 10.22 (1H, s), 4.0 (3H, s), 3.71 (3H, s). MS, *m/e* (%): 488 (M^+, 50), 433 (4), 420 (100), 419 (96), 405 (16), 389 (9), 377 (8), 376 (6), 364 (52), 363 (100), 359 (18), 333 (20), 331 (30), 321 (14).

Hexahydro-ferruginin A. Ferruginin A (100 mg) in MeOH) (5 ml) was hydrogenated over C/Pt 10% (100 mg). Standard work-up and crystallisation from CH_2Cl_2 afforded hexahydroferruginin A, m.p. 200–5° (subl.). UV ($CHCl_3$), λ_{max} 241, 263, 282, 422 nm (log ϵ: 4.45, 4.34, 4.27, 3.98). IR ($CHCl_3$), ν_{max} 3350, 1630, 1610, 1590, 1570 cm^{-1}. PMR (acetone-d_6), δ: 17.75 (1H, s), 10.3 (1H, s), 7.2 (H_{10}, s), 7.05 (H_5, s), 5.83 (H_2, s), 3–2.5 (2H, m), 2.4 (3H, s), 2.35–1.1 (13H, m), 1.0 (6H, d, J Hz), 0.78 (6H, d, J 7 Hz), 0.70 (6H, d, J 7 Hz). MS, *m/e* (%): 466 (M^+, 100), 409 (89), 396 (13), 339 (100), 329 (13), 283 (6), 282 (6), 281 (18), 296 (18): metastable peaks were observed at m* 359 (466→409), m* 336.5 (466→396), m* 290 (396→339), m* 281 (409→339) and m* 213.5 (339→269).

Thermal rearrangement of ferruginin A. Ferruginin A (120 mg) in sublimator was kept at 140° (15 min), then at 170° (10 min) under vacuum (0.04 mmHg). The crude product was purified on a silica-gel column. Methylene chloride eluted successively the anthrone A_1 (10 mg), A_2 (42 mg) and A_3 (55 mg). In other experiments the ratio between the anthrones A_2 and A_3 was reversed depending by the manner of heating. *Anthrone* A_1 (6), brick red crystals, m.p. 146–50° (CH_2Cl_2–heptane). UV ($CHCl_3$), λ_{max} 241, 263, 276, 319, 365 nm (log ϵ: 4.03, 3.92, 3.87, 4.01, 4.09). PMR ($CDCl_3$), δ: 13.15 (1H, s), 12.70 (1H, s), 6.63 (1H, s), 6.2 (1H, s), 5.30–4.83 (3H, m), 4.03 (2H, s), 3.50–3.18 (6H, broad m), 2.3 (3H, s), 1.87–1.68 (18H). With D_2O the peak at δ 6.2 disappears and those at δ 13.15 and 12.70 become less high. PMR (C_5D_5N) in Table 2. MS, *m/e* (%): 460 (M^+, 64), 417 (13), 405 (40), 404 (100), 389 (10), 361 (26), 349 (52), 348 (64), 333 (28), 305 (40), 293 (40): a metastable peak was observed at m* 354.8 (460→404). *Anthrone* A_2, (7 R = R_1 = H), oil. UV ($CHCl_3$), λ_{max} 239, 253, 277, 370 nm (log ϵ: 4.07, 4.03, 3.96, 4.28). IR ($CHCl_3$), ν_{max} 3550, 3200, 1600 cm^{-1}. PMR ($CDCl_3$), δ: 12.63 (1H, s), 12.36 (1H, s), 6.54 (H_5, s), 6.26 (H_2, s), 6.1 (OH, broad s), 5.0 (2H, broad t, J 7 Hz), 4.60 (1H, t, J 7 Hz), 4.20 (1 H, t, J 5 Hz), 3.37 (4H, broad d, J 7 Hz), 2.45–2.15 (2H, m), 2.3 (3H, s), 1.83–1.70 (12H), 1.5 (3H, s), 0.97 (3H, s). Irradiating the multiplet centrated at δ ~2.3, both the triplets at δ 4.6 and 4.2 become broad singlets. PMR (C_5D_5N) in Table 2. MS, *m/e* (%): 460 (M^+, 22), 407 (25), 392 (50), 391 (100), 349 (17), 348 (20), 347 (20), 336 (25), 323 (16), 305 (5), 293 (30), 281 (26), 69 (15): metastable peaks were observed at m* 334 (460→392), m* 311.5 (392→349) and m* 288.7 (392→336). Acetylation with py–Ac_2O overnight at room temperature afforded the *diacetyl-derivative* 7 (R = Ac, R_1 = H): PMR ($CDCl_3$), δ: 12.58 (1H, s), 6.80 (H_2, s), 6.56 (H_5, s), 2.37 (3H, s), 2.30 (6H, s). Acetylation with AcONa–Ac_2O 1h on reflux gave the *triacetyl-derivative* 7 (R = R_1 = Ac): UV ($CHCl_3$), λ_{max}: 243, 285 nm (log ϵ: 4.04, 4.07): PMR ($CDCl_3$), δ: 6.93 (H_5, s), 6.72 (H_2, s), 2.33 (9H, s), 2.23 (3H, s). *Anthrone* A_3, 8, light yellow crystals, m.p. 198–201° (MeOH). UV ($CHCl_3$), λ_{max} 238, 258, 277, 370 nm (log ϵ: 4.11, 4.15, 4.01, 4.25). IR (KBr), ν_{max} 1610–1600 cm^{-1}. PMR ($CDCl_3$–CD_3OD), δ: 12.78 (1/3H, OH, partially exchanged with the solvent), 12.5 (1/3 H, s, OH), 6.3 (H_2, s), 5.0 (3H, broad signal), 3.9 (2H, s), 3.3 (6H, broad d), 2.2 (3H, s), 1.76 (18 H, d, J 8 Hz). PMR (C_5D_5N) in Table 2. MS, *m/e* (%): 460 (M^+, 82), 417 (16), 405 (45), 404 (100), 389 (20), 361 (82), 349 (90), 348 (12), 336 (30), 335 (55), 305 (26), 293 (22), 281 (10): metastable peaks were observed at m* 374.5 (404→389), m* 354.8 (460→404), m* 301.5 (404→349), m* 277.8 (404→335), m* 257.7 (361→305), and m* 246 (349→293). Acetylation with py–Ac_2O overnight at room temperature gave the *tetracetyl-derivative*, 10, m.p. 127–30° (CH_2Cl_2–hexane). UV ($CHCl_3$), λ_{max} 270, 386, 407 nm (log ϵ: 5.0, 3.86, 3.75). IR ($CHCl_3$), ν_{max} 1770–1750, 1620, 1360, 1350, 1170 cm^{-1}. PMR ($CDCl_3$), δ: 8.59 (H_{10}, s), 6.85 (H_2, s), 5.2–4.8 (3H, m), 3.9–3.6 (4H, m), 3.45–3.35 (2H, m), 2.33 (12H), 2.23 (3H, s), 1.83–1.66 (18H).

Cyclisation of the anthrone A_2. The anthrone A_2 (120 mg) was dissolved in TFA (1 ml) and the disappearance of the unsaturated protons at δ ~5.0 was followed by PMR. After 15 min the soln was evaporated and the residue was dissolved in CH_2Cl_2–MeOH–2N NaOH and stirred 1 h at room temp. Acidification with 2N HCl and standard work-up gave the raw product, which was purified on a SiO_2 column. Elution with $CHCl_3$ afforded successively the cyclized anthrones 11 and 12. *Anthrone* 11, oil; UV ($CHCl_3$), λ_{max} 241, 263, 275, 356 nm (log ϵ: 4.11, 4.0, 3.96, 4.16); PMR ($CDCl_3$), δ: 13.13 (1H, s), 6.63 (H_5, s), 6.2 (H_2, s), 4.8 (1H, t, J 7 Hz), 4.03 (H_{10}, t, J 6 Hz), 2.75 and 2.63 (2H each, two partially superimposed t, J 7.5 Hz), 2.3 (2H, d, J 6 Hz), 2.25 (3H, s), 1.88 (2H, t, J 7.5 Hz), 1.83 (2H, t, J 7.5 Hz), 1.5 (3H, s), 1.3 (12H, s), 1.0 (3H, s); MS, *m/e* (%): 460 (M^+, 17), 392 (100), 391 (57), 375 (3), 349 (2), 337 (10), 336 (19), 321 (2), 319 (2), 307 (4), 293 (6), 281 (19). *Anthrone* 12, brown crystals from CH_2Cl_2–heptane, m.p. 102–8°; UV ($CHCl_3$), λ_{max} 241, 262, 276, 355 nm (log ϵ: 4.14, 4.02, 4.0, 4.18). IR ($CHCl_3$), ν_{max}: 3600, 1620 cm^{-1}. PMR ($CDCl_3$), δ: 13.1 (1H, s), 6.63 (H_5, s), 6.20 (H_2, s), 4.01 (H_{10}, t, J 6 Hz), 2.9–2.45 (4H, m), 2.3 (2H, m), 2.23 (3H, s), 2.0–1.7 (6H, m), 1.50 (3H, s), 1.3 (6H, s), 1.23 (3H, s), 1.0 (6H, s); MS, *m/e* (%): 478 (M^+, 48), 392 (39), 391 (100), 349 (2), 337 (2), 336 (8), 321 (1), 319 (1), 307 (2), 293 (3), 281 (12).

Cyclisation of the anthrone A_3. The anthrone A_3 (100 mg) treated as above for 30 min, gave after purification the anthraquinone 13, red-orange crystals (CH_2Cl_2–heptane), m.p. 108–11°. UV ($CHCl_3$), λ_{max} 241, 272, 298 sh, 440 nm (log ϵ: 4.01, 4.12, 3.98, 3.79). IR ($CHCl_3$), ν_{max} 3550, 1620. PMR ($CDCl_3$), δ: 12.95 (1H, s), 6.50 (H_2, s), 3.1 (2H, t, J 7 Hz), 2.75 (2H, t, J 7 Hz), 2.30

(3H, s), 2.2–1.8 (4H, m), 1.9 (4H, t, J 7 Hz), 1.43 (3H, s), 1.37 (9H, s), 1.25 (6H, s). MS, *m/e* (%): 492 (27), 474 (29), 457 (15), 432 (15), 431 (27), 419 (52), 418 (100), 363 (29), 308 (15): metastable peaks were observed at m* 315.2 (418→363), m* 456.1 (492→474) and m* 368.6 (474→418). *Ferruginin B*, 14, Red-orange crystals (heptane), m.p. 110–4°. (Found: (Calc. for $C_{30}H_{36}O_4$): C, 78.15 (78.23), H, 7.72 (7.88)%) UV (EtOH) and IR spectra in Table 1. UV ($CHCl_3$): λ_{max} 242, 261, 411 nm (log *e*: 4.19, 4.0, 3.66). PMR ($CDCl_3$), *δ*: 17.1 (1H, s), 10.0 (1H, broad s), 7.08 (H_{16}, s), 6.93 (H_5, s, long range coupling with C_6–CH_3), 6.62 (H_7, s, long range coupling with C_6–CH_3), 5.08 (1H, t, J 7 Hz), 4.53 (2H, t, J 7 Hz), 3.25 (2H, d, J 7 Hz), 2.93–2.5 (4H, m), 2.35 (3H, s), 1.78 (6H, broads), 1.42 (12H, s). MS, *m/e* (%): 460 (M^+, 27), 404 (17), 392 (100), 391 (56), 375 (22), 361 (6), 349 (25), 348 (17), 336 (68), 335 (70), 324 (21), 323 (25), 321 (17), 319 (19), 305 (15), 293 (90), 292 (23), 281 (54), 280 (94).

Thermal rearrangement of ferruginin B. Ferruginin B (120 mg) in sublimator was kept at 180° (30 min) under vacuum (0.04 mmHg). The product was purified on a silica-gel column with C_6H_6–hexane, 1–2. Anthrones B_1 (8 mg), B_2 (20 mg) and B_3 (85 mg) were successively eluted. The anthrone B_1 resulted identical (tlc, RMN, mixed m.p.) to the anthrone A_1, 6. *Anthrone* B_2, 15, orange crystals (heptane), m.p. 58–60°. UV ($CHCl_3$), λ_{max} 241, 260, 272, 365 nm. IR ($CHCl_3$), ν_{max} 3400, 1620–1600 cm^{-1}. PMR ($CDCl_3$), *δ*: 12.9 (1H, s), 12.1 (1H, s), 6.6 (H_5 and H_7, m), 6.2 (1H, disappears with D_2O), 5.1 (2H, t, J 7 Hz), 4.6 (1H, t, J 7 Hz), 4.2 (H_{16}, t, J 5 Hz), 3.4 (4H, d, J 7 Hz), 2.4 (2H, d, J 7 Hz), 2.32 (3H, s), 1.83–1.70 (12H), 1.52 (3H, s), 0.96 (3H, s). PMR (C_5D_5N) in Table 1. *Anthrone* B_3, 16, light yellow crystals (CH_2Cl_2), m.p. 175–7°. UV ($CHCl_3$), λ_{max} 240, 256, 274, 315, 366 (log *e*: 4.14, 4.06, 3.91, 4.0, 4.20). PMR ($CDCl_3$), *δ*: 13.0 (1H, s), 12.4 (1H, s), 6.63 (H_7, s), 5.3–4.75 (3H, m), 3.92 (2H, s), 3.5–3.2 (6H, m), 2.3 (3H, s), 1.85–1.70 (18H). PMR (C_5D_5N) in Table 1. MS, *m/e* (%): 460 (M^+, 34), 417 (2), 405 (80), 404 (93), 389 (13), 361 (34), 350 (60), 349 (95), 348 (80), 333 (42), 305 (57), 293 (100). Acetylation of the anthrone B_3 with py–Ac_2O overnight at room temp. gave a tetracetyl derivative, amorphous solid; UV ($CHCl_3$), λ_{max} 270, 387, 410 nm; PMR ($CHCl_3$), *δ*: 8.85 (H_{16}, s), 6.90 (H_7, s), 2.45–2.3 (15H).

Ferruginin C (*harunganin*), 3 (R = H). Crude ferruginin C, single spot on tlc, orange crystals (CH_2Cl_2), m.p. 170–5°. PMR spectra in. acetone–d_6 and in C_5D_5N gave evidence for the presence of an impurity: double signals for H_{16}, H_2, H_7 and aromatic Me (only in C_5D_5N), signal at *δ* 7.05 (0.3H, H_5 of the impurity) and integration curve of the prenyl chain on aromatic ring. Two further crystallisations from acetone yielded the pure product (harunganin), orange crystals, m.p. 185–8° (lit.[4b] 190°). UV (EtOH) and IR in Table 1. UV ($CHCl_3$), λ_{max} 242, 323, 412 nm (log *e*: 4.61, 4.06, 4.16). PMR (acetone–d_6), *δ*: 17.2, (1H, s), 10.0 (1H, s), 7.37 (H_{16}, s), 6.63 (H_7, s), 5.83 (H_2, s), 5.02 (1H, t, J 7 Hz), 4.70 (2H, t, J 7 Hz), 3.63 (2H, d, J 7 Hz), 2.9 (4H, heptet), 2.4 (3H, s), 1.92 (3H, s), 1.68 (3H, s), 1.43 (12H, broad s).

Thermal rearrangement of ferruginin C. Ferruginin C, m.p. 170–5°, was kept in sublimator at 150° (20 min) then at 170° (10 min) under vacuum (0.04 mmHg). The crude product was purified on a silica-gel column. Methylene chloride eluted successively the anthrones HR_1 (31 mg), HR_2 (69 mg), HR_3 (25 mg) and HR_4 (34 mg). The anthrones HR_1 and HR_3 resulted identical (tlc, PMR, mixed m.p.) to the anthrones B_3, 16, and A_3, 8, respectively. *Anthrone* HR_2, 5 (R = H), oil. UV ($CHCl_3$), λ_{max} 241, 259, 278, 372 nm (log *e*: 4.02, 3.96, 3.87, 4.12). IR ($CHCl_3$), ν_{max} 3600, 3200, 1600 cm^{-1}. PMR ($CDCl_3$), *δ*: 12.57 (1H, s), 12.30 (1H, s), 6.63 (H_7, s), 6.30 (H_2, s), 5.0 (2H, broad), 4.70 (H_{16}, t, J 5 Hz), 4.50 (1H, t, J 7 Hz), 3.42 (4H, d, J 7 Hz), 2.35 (2H, d, J 7 Hz), 2.30 (3H, s), 1.85–1.70 (12h), 1.50 (3H, s), 0.92 (3H, s). *Anthrone* HR_4, 17, amorphous solid, m.p. 185–97°. UV ($CHCl_3$), λ_{max}: 241, 259, 303, 368 nm (log *e*: 3.95, 3.95, 3.74, 3.99). IR ($CHCl_3$), ν_{max} 3350, 1600 cm^{-1}. PMR ($CDCl_3$–CD_3OD, 4–1), *δ*: 12.67 (0.2H, s, OH, partially exchanged with the solvent), 12.4 (0.2H, s), 6.66 (H_7, s), 6.3 (H_2, s), 5.0 (1H, t, J 7 Hz), 4.87 (1H, t, J 7 Hz), 4.0 (2H, s), 3.50–3.25 (4H, m), 2.30 (3H, s), 1.87–1.70 (12H). Acetylation of the anthrone HR_4 with py–Ac_2O overnight at room temp. gave a tetraacetyl derivative, amorphous solid; UV ($CHCl_3$), λ_{max} 267, 387, 408 nm. PMR ($CDCl_3$), *δ*: 8.63 (H_{16}, s), 6.95 (H_7, s), 6.90 (H_2, s), 2.47 (3H, s), 2.40 (6H, s), 2.36 (3H, s), 2.30 (3H, s).

Ferruanthrone, 18. Yellow-orange crystals (CH_2Cl_2–heptane), m.p. 166–70°. (Found; (Calc. for $C_{30}H_{36}O_4$): C, 78.35 (78.23), H, 7.72 (7.88)%. UV ($CHCl_3$), λ_{max} 240, 256, 275, 313, 365 (log *e*: 4.09, 4.04, 3.94, 3.96, 4.15). IR ($CHCl_3$), ν_{max} 3370, 1610–1590 cm^{-1}. PMR ($CDCl_3$), *δ*: 13.07 (1H, s), 12.43 (1H, s), 6.60 (H_4, s), 6.20 (OH, s, disappears with D_2O), 5.20 (1H, t, J 7 Hz), 5.05–4.65 (2H, m), 3.9 (2H, s), 3.50–3.15 (6H, m), 2.25 (3H, s), 1.80–1.70 (18H). MS, *m/e* (%): 460 (M^+, 40), 405 (31), 404 (100), 389 (9), 387 (18), 361 (25), 349 (59), 348 (62), 338 (27), 336 (15), 333 (24), 323 (14), 319 (11), 309 (15), 305 (33), 295 (49), 293 (50), 292 (33), 283 (42), 282 (73), 280 (19). Acetylation of ferruanthrone with py–Ac_2O overnight at room temp. gave a tetraacetyl derivative, m.p. 110–6° (CH_2Cl_2–hexane); UV ($CHCl_3$), λ_{max} 271, 384, 409 nm; IR ($CHCl_3$), ν_{max} 1770–50, 1620, 1360, 1170 cm^{-1}; PMR ($CDCl_3$), *δ*: 8.58 (H_{16}, s), 6.91 (H_4, s), 2.40 (6H, s), 2.33 (6H, s).

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