CHEMISTRY OF *VISMIA* GENUS. NOTE V: γ-HYDROXY- AND γ,γ'-DIHYDROXY-FERRUGININ A

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ABSTRACT.—The chemical composition of the berries of three *Vismia* species is reported. The structure of two new prenylated anthranoids was determined by spectroscopic methods and by hydrogenolysis to hexahydro ferruginin A. The thermal rearrangement to anthrones was also accomplished. The hydroxylation of one of the prenyl chains is rather unusual in natural products.

In previous papers we have reported the structure determination of new prenylated anthranoids, vismiones and ferruginins isolated from five species of the genus *Vismia* (Guttiferae): i.e. *V. baccifera* var. *dealbata* (1, 2), *V. baccifera* var. *ferruginea* (3), *V. macrophylla* (4), *V. lindeniana* (4), and *V. falcata* (4). The interesting chemical structures of these products prompted us to investigate other species of the same genus.

This paper will deal with the results obtained from the examination of three further species: *V. guaramirangae*, *V. decipiens* and *V. guianensis*, the former two from Brazil and the latter from Columbia.

The three species, as observed by Ewan in his botancial synopsis on this genus (5), are closely related; in the present chemical study, we found also a similar qualitative composition. In fact, all contain the previously known ferruginin A, (**1**) ($C_{30}H_{36}O_4$), and two new optically active compounds, $C_{30}H_{36}O_5$ and $C_{30}H_{36}O_6$, respectively. The ir, uv and visible spectra of both the compounds show closer similarity to those of ferruginins (3) rather than to those of vismiones (2).

The fragmentation in the mass spectrum of the former ($C_{30}H_{36}O_5$), named γ-hydroxyferruginin A, suggests that the extra oxygen atom is contained in one of the two gem-C-prenyl chains.

A comparison in two different solvents of the chemical shifts of both the aromatic protons and of the methylene of the prenyl chain on the aromatic ring (tab. 1) established the latter to be at C_7. Also the $\Delta\delta$ value of the methylene agrees with this location.

Final proof was obtained by catalytic hydrogenation of γ-hydroxyferruginin A, which gave hexahydroferruginin A (**5**) ($C_{30}H_{42}O_4$) (3) with loss of an oxygen atom by hydrogenolysis.

This finding suggested also that this oxygen is part of an allylic hydroxyl (6). On the other hand, the pmr spectrum (acetone-d_6) of γ-hydroxyferruginin A showed *only five* unsaturated methyl signals and one two proton singlet at δ 3.66 which shifted to δ 4.14 and 4.13 in the dimethylmonoacetyl- and dimethyldiacetyl-derivatives, respectively.

On the basis of the above data, the structure **6** can be assigned to γ-hydroxyferruginin A; the presence of the γ-hydroxymethyl-γ'-methyallyl chain accounts for its optical rotation.

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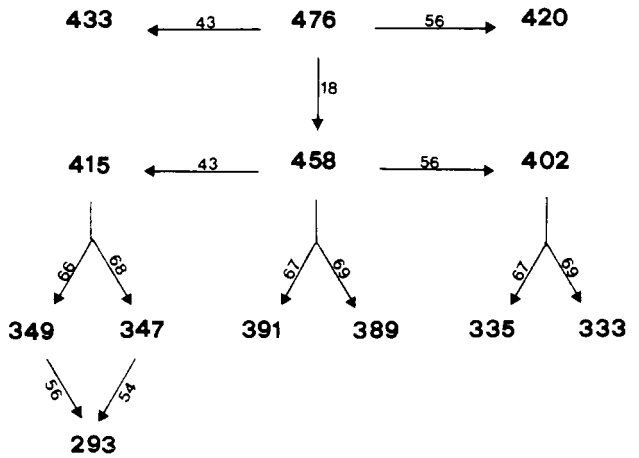
TABLE 1. Pmr spectra of ferruginins in pyridine-d_5[0] and in acetone-d_6[00].

	C_2	C_5	C_7	C_{10}
Vismin (4), **2**	6.12 5.80	7.06 7.05	6.76 6.60	7.50 7.32
Ferruginin B (3), **3**	3.53 3.12	7.06 7.0	6.77 6.55	7.44 7.30
	Δδ*0.41			
Harunganin (3), **4**	6.13 5.83	3.66 3.63	6.83 6.63	7.63 δ7.46
		Δδ*0.03		
Ferruginin A, (3) **1**	6.13 5.77	7.15 7.02	3.62 3.43	7.47 7.24
			Δδ*0.19	
γ-Hydroxyferruginin A, **6**	6.10 5.76	7.13 7.05	3.63 3.43	7.48 7.30
			Δδ*0.20	
γ,γ'-Dihydroxyferruginin A, **11**	6.13 5.77	7.10 7.06	3.63 3.43	7.50 δ7.30
			Δδ*0.20	

[0]First value.
[00]Second value.
*$\Delta\delta = \delta\ C_5D_5N - \delta\ CD_3COCD_3$ of the methylene of the prenyl chain on the aromatic ring.

In the mass spectrum of γ-hydroxyferruginin A, the ion at *m/e* 458 (base peak) can be explained by 1,2- or 1,4 elimination of a molecule of water from the oxygenated chain; successively, it loses 43 or 56 mu (due to the prenyl on the aromatic ring), and 56 or 68/69 mu (due to the γ,γ'-dimethylallyl chain at C_4), like ferruginins (3, 7) and similar compounds (8). In addition, losses of 54 or 66/67 mu (due to the dehydrated prenyl chain at C_4) can be observed (scheme 1).



SCHEME 1

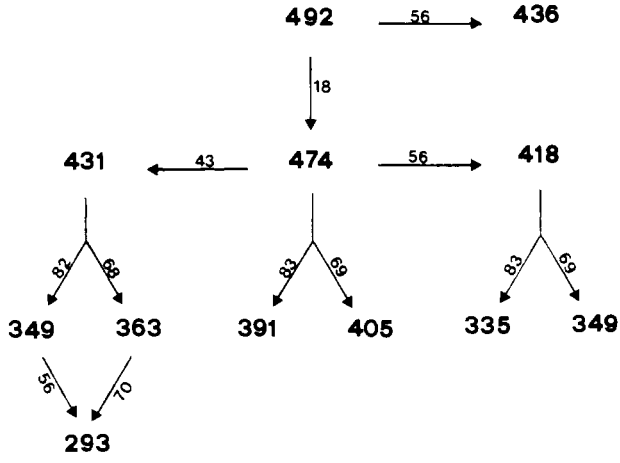
γ-Hydroxyferruginin A, like ferruginins (4, 3), on heating gives many products of isomerization. Only the most abundant one, γ-hydroxy anthrone A_3, was submitted to structure determination.

According to a previously described (3) method, from the pmr spectrum in pyridine-d_5 it is possible to distinguish a γ,γ'-dimethylallyl chain on C_2 (between two hydroxyls), one on C_4 or C_7 (adjacent to one hydroxyl) and one on C_5 (without adjacent hydroxyl). The pmr spectrum of γ-hydroxy anthrone A_3 showed a prenyl on C_5 (δ 4.98, 1H; δ 3.42, 2H) and *only one* on C_7 or C_4 (δ 5.32, 1H; δ 3.62, 2H). Assuming that the prenyl on C_7 in **6** does not suffer shift, it follows that the structure of γ-hydroxy anthrone A_3 is **10**.

The second compound ($C_{30}H_{36}O_6$) isolated from *Vismia* species, now named γ,γ'-dihydroxyferruginin A, showed in the pmr spectrum *only four* unsaturated methyl signals and two two-proton singlets (δ 4.70 and 3.85, respectively, in acetone-d_6), attributed to two hydroxymethyl groups.

The presence of a γ,γ'-dimethylallyl chain at C_7, as in ferruginin A (**1**) and in γ-hydroxyferruginin A (**6**), was established on the basis of the chemical shifts both of the aromatic protons and of the methylene of this chain (table 1). This location was confirmed by the hydrogenation/hydrogenolysis, which gave hexahydroferruginin A (**5**) ($C_{30}H_{42}O_4$). The loss of two hydroxyls by hydrogenolysis suggested again their allylic nature, moreover the hydroxyls may belong respectively to the two prenyl chains in C–4 or they can both be bonded to a single chain.

The fragmentation in the mass spectrum of γ-γ'-dihydroxyferruginin A (scheme 2) is analogous to that of γ-hydroxyferruginin A (scheme 1) with most of the ions



SCHEME 2

shifted by 16 mu. Notably the losses from the ion *m/e* 474 ($M^+ - 18$) of 68/69 or 82/83 (=–CH=CH–C(CH_2OH)=CH_2) established that both the hydroxyls are part of the same chain. Consequently the structure of γ,γ'-dihydroxyferruginin A is **11**.

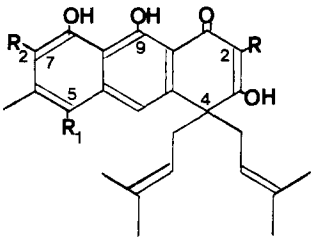
From the hydrogenation/hydrogenolysis of γ,γ'-dihydroxyferrugin A, two other isomeric compounds ($C_{30}H_{42}O_5$) could be isolated by extensive fractionation.

To these products the structure **12** (epimers at the γ-position of the oxygenated chain) was assigned and their formation may be explained by hydrogenation of the double bond before the hydrogenolysis of the second hydroxyl. The same

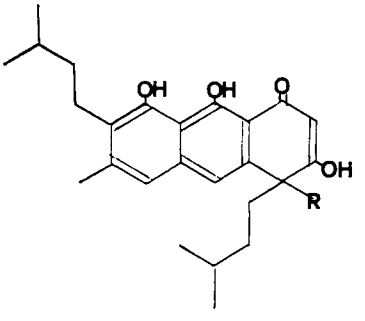
two products were found, as minor components, in the hydrogenation mixture of γ-hydroxyferruginin A (**6**).

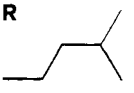
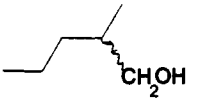
By brief heating at 100° under vacuum, γ,γ'-dihydroxy ferruginin A (**11**) rearranges to give several anthrones. On the basis of the pmr spectrum in C_5D_5N, structure **13** was assigned to the most abundant anthrone ($C_{30}H_{36}H_6$, m^+ at *m/e* 492), indicated as γ,γ'-dihydroxyanthrone A_3.

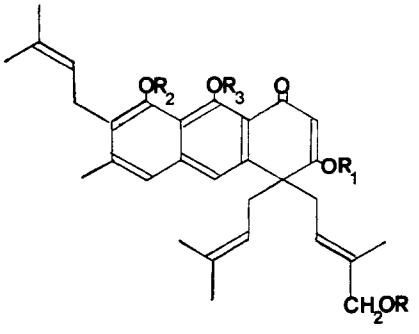
A second product ($C_{30}H_{36}O_6$, M^+ at *m/e* 492), indicated as γ,γ'-dihydroxy anthone A_2, showed in the pmr spectrum *two* aromatic protons and a γ,γ'-dimethylallyl chain at C_{10}, particularly evidenced by the unusual chemical shift (3) of the allylic methyl signals (δ 1.53 and 1.03) and confirmed by a loss of 69 mu



	R	R_1	R_2
1	H	H	Pr
2	H	H	H
3	Pr	H	H
4	H	Pr	H



	R
5	
12	



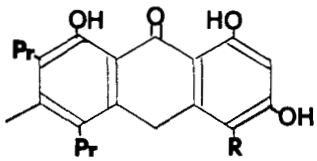
	R	R_1	R_2	R_3
6	H	H	H	H
7	H	CH_3	H	CH_3
8	Ac	CH_3	H	CH_3
9	Ac	CH_3	Ac	CH_3

Pr=isoprenyl

from the molecular ion in the mass spectrum. Consequently the structure **14** was assigned to γ,γ'-dihydroxyanthrone A_2.

These findings prove that dihydroxyferruginin A, like ferruginins (3), rearranges to anthrone, where the "lighter" chain at C_4 shifts to C_5 or C_{10}.

Two other less polar products could be obtained in higher yield by prolonged heating at 180–200°. Because of the close Rf value, they could be separated only by preparative tlc. On the basis of the pmr spectrum ($CDCl_3$) where a



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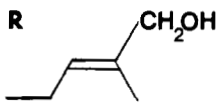

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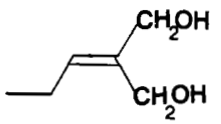

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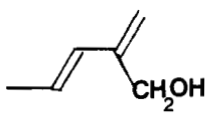

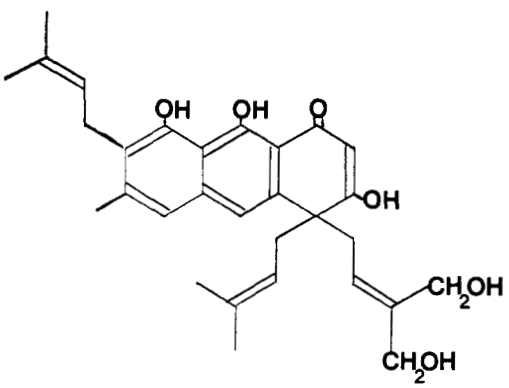

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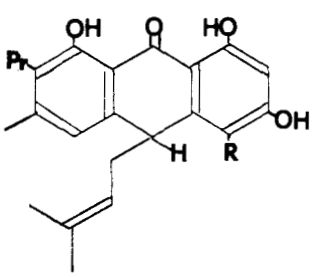

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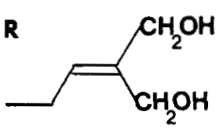

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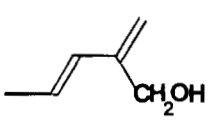

γ,γ'-dimethylallyl chain at C_{10} (unsaturated methyl signals at δ 1.55 and 1.05), *two* aromatic protons and *only one* hydroxymethyl group (δ 4.30) are exhibited, structure **15** was assigned to the first one (M^+ at *m/e* 474 instead of 492). In a similar way (see experimental), structure **16** was attributed to the second compound (M^+ at *m/e* 474 instead of 492).

In order to prove this structure, γ,γ'-dihydroxy anthrone A_3 (**13**) was heated (3 hours) nearly to the melting point; the anthrone **16** was obtained as the main product.

γ-Hydroxyferruginin A (**6**) was also found in *V. falcata* and *C. lindeniana*; γ,γ'-dihydroxyferruginin A (**11**) was found only in the latter (4). They represent two new members of the family of the ferruginins, in particular they may be originated from ferruginin A (**1**) by oxidation of one or two allylic methyls of the same prenyl chain at C_4.

To our knowledge the γ,γ'-dihydroxymethylallylic chain has not been previously found in natural products, while the γ-hydroxymethyl-γ'-methylallylic chain is quite unusual, the only two examples being lomatiol (9) and oxyguanandin (10), a 2-hydroxynaphthoquinone and a 1,5-dihydroxy xanthone, respectively.

EXPERIMENTAL[2]

PLANT MATERIAL.—The berries of *Vismia guaramirangae* Huber, syn. *V. reichardtiana* (Kuntze) Ewan, comb. nov., syn. *V. guttifera* Salzm., syn. *V. baccifera* var. *augustifolia* Reich., syn. *V. cearensis* Huber, were collected in January 1978 in Brazil (serra de Pacatuba, near Fortaleza, Ceara) and identified by Dr. J. Matos. A voucher sample is in the Herbarium of CCR (Centro Chimica Recettori del CNR) under the cipher RAL N. 1.

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

The berries of *V. guianensis* (Aubl.) Choisy, syn. *V. caparosa* H.B.K., syn. *V. acuminata* var. *caparosa* Choisy, were collected in June 1978 in Columbia (Dept. of Boyacá; road from Santa Maria to San Luis de Gaceno; shores of Rio Legupá; alt. 520 m) and identified by Dr. R. Jaramillo (Depto de Botanica, Universidad Nacional, Bogotá). A voucher sample is deposited in the Herbario Nacional de Colombia under the cipher LECS N. 3.

The berries were extracted twice with cold chloroform to give a dark orange grease after removal of the solvent. A portion was purified on a silica gel column: elution with chloroform yielded: (a) a mixture of sesquiterpenes and triglycerides; (b) ferruginin A; (c) fatty acids. Further elution with chloroform-methanol, 95:5, gave γ-hydroxyferruginin A and γ,γ'-dihydroxyferruginin A, successively. The approximate yield (g/kg) of each pigment from the three species of *Vismia* were: *V. guaramirangae* (0.4; 19; 2), *V. decipiens* (5; 14; 4) and *V. guianensis* (1; 36; 15). In the triglycerides/sesquiterpenes mixture from *V. decipiens* two other unidentified pigments were present.

The juice of the berries of *V. guaramirangae* was also analyzed. A mixture of ferruginins was directly obtained after filtration: lyophilization of the water gave the following sugars (15% of the berries) identified by paper co-chromatography: glucose, fructose, lactose and inositol.

γ-HYDROXYFERRUGININ A (**6**).—The compound crystallized as red-orange crystals from hexane, m.p. 82–4°; $[\alpha]_D = +59$ (c 0.97, $CHCl_3$). Elem. anal., found % (calc. for $C_{30}H_{36}O_5$): C 75.51 (75.69); H 7.72 (7.61). It gave the following additional data: uv (EtOH), λ max: 245, 322, 337 sh, 410 nm; uv ($CHCl_3$), λ max: 245, 261, 280, 418 nm (lg ε: 4.55, 4.31, 4.24, 3.95); pmr (acetone-d_6), δ: 17.70 (1H, s), 10.35 (1H, s), 7.30 (H_{16}, s), 7.05 (H_5, s, long-range coupling with C_6–CH_3), 5.76 (H_2, s), 5.10 and 4.95 (2H, two partially overlapped t, *J* 7 Hz), 4.62 (1H, t, *J* 7 Hz), 3.64 (2H, s), 3.43 (2H, d, *J* 7 Hz), 2.90 (4H, m), 2.37 (3H, s), 1.78 (3H, s), 1.64 (3H, s), 1.45 (9H, broad s); pmr (C_5D_5N), δ: 7.48 (H_{16}, s) and 7.13 (H_5, s) overlapped to solvent signals, 6.10 (H_2, s), 5.60 (1H, t, *J* 7 Hz), 5.30 (1H, t, *J* 7 Hz), 5.04 (1H, t, *J* 7 Hz), 4.03 (2H, s), 3.63 (2H, d, *J* 7 Hz), 3.24 (2H, m), 3.07 (2H, m), 2.40 (3H, s), 1.80 (6H, s), 1.68 (3H, s), 1.60 (3H, s), 1.43 (3H, s). Decoupling experiments established the following couplings: δ 5.60 (t) with

[2]Uv spectra were recorded on a Beckman Acta III, ir spectra on a Perkin Elmer 247, mass spectra on an AEI 12, and pmr spectra on a Varian EM 360 spectrometer (TMS as internal standard: s = singlet, d = doublet, t = triplet, m = multiplet).

SiO_2 MN Kieselgel was used for column chromatography and Kieselgel 60 F_{254} for tlc. Melting points were obtained on a Kofler apparatus and are uncorrected. For [α] a Perkin Elmer 141 instrument was used.

δ 3.24 (m); δ 5.30 (t) with δ 3.63 (d); δ 5.04 (t) with δ 3.07 (m). Ms, *m/e* (%): 476 (M^-, 100), 458 (100), 433 (7), 420 (44), 415 (44), 403 (50), 402 (63), 391 (29), 389 (27), 387 (12), 377 (20), 365 (14), 361 (16), 359 (29), 349 (24), 347 (27), 336 (19), 335 (15), 333 (10), 319 (7), 305 (9), 293 (10).

METHYLATION OF γ-HYDROXYFERRUGININ A WITH CH_2N_2.—To γ-hydroxyferruginin A (300 mg) in CH_2Cl_2 an excess of CH_2N_2 in ether was added. The mixture was left to stand overnight, then the solvent was evaporated. The residue was passed down a silica gel column eluted with ethyl acetate-chloroform-heptane (1:1:1). Only two products, 3,9-dimethyl-γ-hydroxyferruginin A (100 mg) and 1,9-dimethyl-iso-γ-hydroxyferruginin A (50 mg) were obtained pure.

3,9-DIMETHYL-γ-HYDROXYFERRUGININ A (**7**).—An oil. Uv (EtOH), λ max: 235, 269, 390 nm (lg ε: 4.58, 4.49, 3.85). Pmr ($CDCl_3$), δ: 10.2 (1H, s), 7.53 (H_{10}, s), 7.09 (H_8, s), 5.75 (H_2, s), 4.0 (3H, s), 3.73 (3H, s), 3.70 (2H, s). Ms, *m/e* (%): 504 (M^-, 32), 486 (18), 471 (9), 448 (6), 436 (60), 435 (66), 420 (86), 419 (72), 417 (45), 405 (22), 403 (31), 394 (12), 391 (18), 389 (15), 379 (100), 377 (78), 363 (97), 361 (86), 349 (28). By acetylation (Ac_2O/py) it gave two oily derivatives. The mono-acetyl-derivative (**8**) gave pmr ($CDCl_3$), δ: 10.23 (1H, s, OH), 7.50 (H_{10}, s), 7.06 (H_5, s), 5.73 (H_2, s), 4.14 (2H, s), 4.02 (3H, s), 3.72 (3H, s), 2.42 (3H, s), 1.90 (3H, s, Ac). The diacetyl-derivative (**9**) gave pmr ($CDCl_3$), δ: 7.52 (H_{10}, s), 7.42 (H_5, s), 5.73 (H_2, s), 4.13 (2H, s), 3.90 (3H, s), 3.72 (3H, s), 2.40 (3H, s), 2.36 (3H, s, Ac), 1.89 (3H, s, Ac).

1,9-DIMETHYL-ISO-γ-HYDROXYFERRUGININ A.—The compound was an oil. It gave uv (EtOH), λ max: 243, 304, 387 nm (lg ε: 4.50, 4.22, 3.81); pmr ($CDCl_3$), δ: 10.0 (1H, s), 7.43 (H_{10}, s), 7.06 (H_5, s), 5.70 (H_2, s), 3.93 (3H, s), 3.90 (3H, s), 3.70 (2H, s); ms, *m/e* (%): 504 (M^-, 38), 486 (38), 471 (4), 436 (42), 435 (38), 434 (30), 420 (76), 419 (100), 418 (80), 404 (36), 403 (45), 391 (22), 389 (15), 377 (19), 376 (22), 375 (28), 367 (15), 365 (26), 363 (29), 361 (30), 360 (27), 347 (35).

CATALYTIC HYDROGENATION OF γ-HYDROXYFERRUGININ A.—γ-Hydroxyferruginin A (210 mg) in methanol (10 ml) was hydrogenated over Pt (from 100 mg PtO_2). Standard work-up afforded a mixture, which on a silica gel column with chloroform gave hexahydroferruginin A (95 mg); with 2% ethanol in chloroform gave, successively, hexahydro γ-hydroxyferruginin A, isomer A (65 mg) and isomer B (35 mg).

HEXAHYDROFERRUGININ A (**5**).—The compound gave a mp and mixture mp 200–3°, pmr and ir spectra superimposable with those of authentic specimen (3).

HEXAHYDRO-γ-HYDROXYFERRUGININ A (**12**) ISOMER A.—The compound gave a mp 199–202° (CH_2Cl_2); $[\alpha]^{25}D$ −20° (c=0.6, $CHCl_3$); pmr (acetone-d_6), δ: 3.26 (2H, d, *J* 5.5 Hz); ms, *m/e* (%): 482 (M^-, 60), 425 (18), 412 (12), 411 (23), 396 (20), 395 (8), 393 (8), 355 (8), 339 (18), 340 (100), 283 (16), 281 (33), 269 (17), 253 (9).

HEXAHYDRO-γ-HYDROXYFERRUGININ A (**12**) ISOMER B.—The compound gave a mp 140–5° (hexane); $[\alpha]^{25}D$ −64° (c=0.7, $CHCl_3$); pmr (acetone-d_6), δ: 3.18 (2H, d, *J* 5.5 Hz); ms, *m/e* (%): 482 (M^-, 97), 425 (14), 412 (15), 411 (41), 396 (20), 395 (9), 393 (9), 355 (7), 339 (24), 338 (100), 283 (17), 281 (32), 269 (23), 253 (12). The fragmentation of both isomers A and B, characterized by successive losses of the three different C_5 chains, is in agreement with the literature (3, 7).

THERMAL REARRANGEMENT OF γ-HYDROXYFERRUGININ A.—γHydroxyferruginin A (1 g) was kept at 150° under vacuum (0.04 mm Hg) for 1 hr. The crude product in a little chloroform was filtered to give γ-hydroxyanthrone A_3 (0.5 g). The mother liquor was purified on a silica gel column to give the further product (0.1 g).

γ-HYDROXYANTHRONE A_3 (**10**).—The compound appeared as yellow-green crystals, mp 231–5° (MeOH). Elem. anal., found % (calc. for $C_{36}H_{36}O_5$): C 75.72 (75.60); H 7.55 (7.61). It gave the following data: uv ($CHCl_3$), λ max: 241, 261, 277, 309, 366 nm (lg ε: 4.38, 4.36, 3.93, 4.09, 4.20); ir (KBr), ν max: 1610–1600 cm^{-1}; pmr (C_5D_5N), δ: 13.47 (1H, s), 13.17 (1H, s), 6.75 (H_2, s), 5.85 (1H, t, *J* 7 Hz), 5.32 (1H, t, *J* 7 Hz), 4.98 (1H, t, *J* 7 Hz), 4.30 (2H, s), 4.15 (2H, s), 3.75 (2H, d, *J* 7 Hz), 3.62 (2H, d, *J* 7 Hz), 3.42 (2H, d, *J* 7 Hz), 2.32 (3H, s), 2.07 (3H, broad s), 1.85–1.72 (12 H); ms, *m/e* (%): 476 (M^+, 65), 458 (100), 420 (8), 415 (20), 404 (25), 403 (65), 402 (35), 387 (7), 377 (19), 365 (10), 361 (10), 359 (77), 349 (16), 348 (16), 347 (50), 343 (12), 335 (7), 333 (11), 319 (6), 317 (8), 314 (12), 305 (20), 303 (5).

γ,γ'-DIHYDROXYFERRUGININ A (**11**).—It crystallized as red-orange crystals from cyclohexane, mp 107–10°; $[\alpha]D$ = −58 (c=0.61, $CHCl_3$). Elem. anal., found % (calc. for $C_{36}H_{36}O_6$): C 73.25 (73.14); H 7.31 (7.37). It gave the following additional data: uv (EtOH), λ max: 245, 322, 337 sh, 410 nm; uv ($CHCl_3$), λ max 245, 261, 281, 420 (lg ε: 4.54, 4.32, 4.27, 3.95); pmr (acetone-d_6), δ: 17.70 (1H, s), 10.33 (1H, s), 7.30 (H_{10}, s), 7.06 (H_5, s, long-range coupling with C_6–CH_3), 5.77 (H_2, s), 5.13 and 5.0 (2H, two partially overlapped t, *J* 7 Hz), 4.63 (1H, t, *J* 7 Hz), 4.07 (2H, s), 3.85 (2H, s), 3.43 (2H, d, *J* 7 Hz), 3.25–2.70 (2H, m), 2.37 (3H, s), 1.80 (3H, s), 1.63 (3H, s), 1.45 (6H, broad s); pmr (C_5D_5N), δ: 7.50 (H_{10}, s), 7.10 (H_5, s), 6.13 (H_2, s), 5.87 (1H, t, *J* 7 Hz), 5.63 (1H, t, *J* 7 Hz,) 5.05 (1H, t, *J* 7 Hz), 4.70 (2H, s), 4.47 (2H, s), 3.63 (2H, d, *J* 7 Hz), 3.40-2.90 (4H, m), 2.42 (3H, s), 1.83 (3H, s), 1.70 (3H, s), 1.58 (3H, s), 1.43 (3H, s). Decoupling experiments established the following coupling: δ 5.36 (t) with δ 3.63 (d). Ms, *m/e* (%): 492 (M^-, 20), 474 (64), 436 (9), 431 (32), 419 (41), 418 (61), 405 (100), 391 (50), 387 (52), 375 (70), 363 (45), 350 (34), 349 (82), 347 (41), 337 (32), 336 (34), 335 (32), 334 (23), 331 (32), 319 (68), 305 (41), 293 (35).

CATALYTIC HYDROGENATION OF γ,γ'-DIHYDROXYFERRUGININ A.—γ,γ'-Dihydroxyferruginin A (200 mg) in methanol (6 ml) over Pt (from 150 mg PtO_2). Standard work-up and chromatographic separation gave hexahydroferruginin A (55 mg), hexahydro-γ-hydroxyferruginin A, isomer A (70 mg) and isomer B (62 mg). The three compounds gave the same physical and spectroscopic data above reported.

THERMAL REARRANGEMENT OF γ,γ'-DIHYDROXYFERRUGININ A.—γ,γ'-Dihydroxyferruginin A (500 mg) was kept at 100° under vacuum (0.04 mmHg) for 30'. The crude product was purified on a silica gel column to give γ,γ'-dihydroxyanthrone A_3 (280 mg) and A_2 (80 mg). From an experiment at 180–200° for 2 hr and preparative tlc, also the dehydro anthrones **15** and **16** could be obtained.

γ,γ'-DIHYDROXYANTHRONE A_3 (**13**).—The compound crystallized as yellow crystals, mp 225–8°, (CH_2Cl_2–MeOH). Elem. anal., found % (calc. for $C_{30}H_{36}O_6$): C 73.20 (73.14); 7.31 (7.37). Additional data was: uv ($CHCl_3$), λ max: 243, 259, 277, 308, 371 nm; ir (KBr), ν max 1600 cm^{-1}; pmr (C_5D_5N), δ: 13.42 (1H, s), 13.15 (1H, s), 6.75 (H_2, s), 6.05 (1H, t, *J* 7 Hz), 5.30 (1H, t, *J* 7 Hz), 5.03 (1H, t, *J* 7 Hz), 4.92 (2H, s), 4.68 (2H, s), 3.88 (2H, d, *J* 7 Hz), 3.65 (2H, d, *J* 7 Hz), 3.48 (2H, d, *J* 7 Hz), 2.33 (3H, s), 1.90 (3H, s), 1.83 (3H, s), 1.75 (3H, s), 1.70 (3H, s). Decoupling experiments established the following couplings: δ 6.05 (t) with δ 3.88 (d); δ 5.30 (t) with δ 3.65 (d); δ 5.03 (t) with δ 3.48 (d). Ms, *m/e* (%): 492 (M^+, 25), 474 (100), 431 (41), 419 (54), 418 (81), 416 (18), 406 (20), 405 (39), 403 (18), 391 (42), 387 (33), 375 (40), 363 (21), 361 (12), 349 (50).

γ,γ'-DIHYDROXYANTHRONE A_2 (**14**).—The compound was a yellow oil. It gave the following data: pmr ($CDCl_3$), δ: 12.70 (1H, s), 12.50 (1H, s), 6.60 (H_5, s), 6.23 (H_2, s), 5.10–4.65 (3H, m), 4.15 (H_{10}, 1H, t, *J* 5 Hz), 4.0 (2H, s), 3.95 (2H, s), 3.50–3.30 (4H, m), 2.45–2.20 (2H, m), 2.30 (3H, s), 1.78 (3H, s), 1.68 (3H, s), 1.53 (3H, s), 1.03 (3H, s); pmr (C_5D_5N), δ: 6.70 (H_2, s), 6.53 (H_5, s); ms, *m/e* (%): 492 (M^+, 17), 424 (42), 423 (M^+–69, 100), 405 (25), 389 (13), 380 (34), 368 (17), 361 (9), 327 (34), 299 (51), 293 (17), 285 (34), 284 (42), 69 (100).

DEHYDROANTHRONE **15**.—The compound was a yellow oil. It gave the following data: uv ($CHCl_3$), λ max: 241, 260, 280, 370 nm; pmr ($CDCl_3$), δ: 12.77 (1H, s), 12.57 (1H, s), 6.61 (H_5, s), 6.32 (H_2, s), 5.6–5.0 (5H, m), 4.70 (1H, t, *J* 7 Hz), 4.30 (2H, s, CH_2-OH), 3.97 (H_{10}, 1H, t, *J* 5 Hz), 3.50–3.25 (4H, m), 2.50–2.30 (2H, m), 2.33 (3H, s), 1.82 (3H, s), 1.72 (3H, s), 1.55 (3H, s), 1.05 (3H, s); pmr (C_5H_5N), δ: 6.70 (H_2, s), 6.58 (H_5, s); ms, *m/e* (%): 474 (M^+, 20), 406 (42), 405 (100), 389 (4), 387 (7), 377 (6), 362 (23), 350 (15), 331 (8), 319 (5), 293 (4), 280 (6), 69 (20).

DEHYDROANTHRONE **16**.—It crystallized as yellow-orange crystals, mp 178–9°, (CH_2Cl_2–heptane). Additional data were: uv ($CHCl_3$), λ max: 241, 261, 278 sh, 308, 367 nm; pmr (C_5D_5N), δ: 6.58 (H_2, s), 5.80–5.10 (5H, m), 5.02 (1H, t, *J* 7 Hz), 4.50 (2H, s, CH_2OH), 3.90 (2 H_{10}, s), 3.62 (2H, d, *J* 7 Hz), 3.38 (2H, d, *J* 7 Hz), 2.35 (3H, s), 1.87 (6H, s), 1.70 (6H, s); pmr ($CDCl_3$), δ: 12.95 (1H, s), 12.85 (1H, s), 6.23 (H_2, s); ms, *m/e* (%): 474 (M^+, 18), 431 (12), 419 (12), 418 (13), 416 (7), 406 (25), 405 (38), 403 (7), 391 (8), 387 (7), 375 (11), 363 (10), 349 (100). Dehydro anthrone **16** was also obtained from S,S,'-dihydroxyanthrone A_3 (**13**) by heating at 200–220° for 3 hours.

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