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PSOROLACTONES AND OTHER METABOLITES FROM PSOROSPERMUM GLABERRIMUM*

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Abstract - The chemical reactions supporting the structure elucidation of psorolactone A (1), isolated from Psorospermum glaberrimum, are described. The new psorolactone B (5), homoferruginin B (6), 2-prenylphyscion anthrone (7), 6-O-acetyltorosachrysone (8) and 6-O-prenylvismione E (9) were also identified in the extract.

Following our chemosystematic investigation on the secondary metabolites of the tribe of Vismieae (fam. Guttiferae, subfam. Hypericoideae), we have examined the berries of Psorospermum glaberrimum, collected in Ivory Coast. Together with several known anthracene derivatives, characteristic of the tribe [1], we isolated as the main constituent a new type of prenylated anthranoid [2], which featured a lactone ring. The compound, $C_{20}H_{20}O_4$ (1), gave a monomethyl derivative 1a (with CH_2N_2), a dimethyl derivative 1b (with Me_2SO_4) and a diacetyl derivative 1c (with pyr/Ac_2O). The methyl derivatives were used as substrates for chemical reactions, which confirmed the assigned structure and in particular the presence of the unusual lactone ring. When compound 1a was treated with TFA, the products 2 and 3 were obtained, both displaying in ^1H and ^{13}C NMR spectra the signals for an α,α,β-trimethyldihydrofuran ring. Notably, in compound 3 a modification of the lactone moiety to a 2-methylcyclopentanone ring had occured and a reasonable mechanism for this ring contraction has been presented [2]. Conversely, hydrogenation in AcOH of compound 1b gave 4 (R=H), isolated as the methylester 4(R=Me), where the lactone ring had been opened by the effect of the acid and reduced by hydrogenation/hydrogenolysis.

Now also the ^1H NMR spectrum of a second component $C_{20}H_{18}O_5$ (5, M^+ 338), displayed the presence of both the α,α-dimethylallyl chain and the lactone ring, but showed the signals of only one chelated OH (δ 12.63) and two singlet aromatic protons (δ 7.18 and 6.73, respectively). A novel band at 1730 cm^{-1} in the IR spectrum of 5, as compared with that of 1, two carbon signals at δ 189.9 and 184.4 in the ^{13}C NMR spectrum and a longer wavelength absorption (520 nm), suggested the presence of a quinonoid moiety. Therefore the structure of the new anthranoid was formulated as 5. In confirmation the methylderivative 5a was coincident with the product afforded by TTN/celite oxidation [3] of 1a. Compounds 1 and 5 were named psorolactone A and B, respectively. Their biogenetic correlation with the vismiones has been previously discussed [2].

*Part 7 in the series "Chemistry of Psorospermum genus". For part 6 see: G. Delle Monache, B. Botta, J. Oguakwa, and F. Delle Monache, Bull. Chem. Soc. Ethiop. 1(1), 42 (1987).

Four other new metabolites were isolated from the extract. The first, $C_{35}H_{44}O_4$ (6), showed UV and IR data superimposable to those of ferruginin B[4], $C_{30}H_{36}O_4$ (6a). The difference of C_5H_8 in the molecular formula suggested the presence of a C_{10} instead of a C_5 chain in 6, as it was confirmed by comparison of ^1H and ^{13}C NMR spectra. The absence of the characteristic H-2 signal[1] in the ^1H NMR spectrum of 6 supported the same substitution pattern as 6a. In the mass spectrum of 6 the losses of 43,55 and 56 mu from both M^+ and $M - C_{10}H_{16}^{1+}$ are typical of a prenyl chain on a sp^2 carbon[5] and thus the geranyl chain was located on C-4. Because of its instability, no further study was possible on this compound, for which we propose the name of homoferruginin B.

The spectral data of a second metabolite, $C_{21}H_{22}O_4$ (7), showed a close relationship with those of the anthrone 7a obtained by rearrangment of vismione A[6], only the signals of the C-2 substituent in the ^1H NMR spectrum being different; it was thus assigned the structure of 2-prenylphyscion anthrone (7), whose biogenetic correlation with vismione E[7] (vide infra) is evident.

The ^1H NMR spectrum of a third pigment, $C_{16}H_{18}O_6$ (1), resembled in the low field region that of torosachrysone[8] (8a). It was completed by the signals of an acetyl group and of four aliphatic protons, which showed up as an AB system, whereas the C-5 and C-7 methylene protons of torosachrysone give broad singlets. This difference in the splitting pattern has been correlated to the presence or absence of a 6-O-acetyl group[1]. The losses of AcOH and H_2O from M^+ in the mass spectra of 8 and torosachrysone, respectively, yielded the same ion (at m/z 270) and the same fragmentation. The new compound was thus assigned the structure 8 and the name of 6-O-acetyltorosachrysone.

The fourth metabolite, $C_{26}H_{32}O_5$ (9), and vismione E[7] (9a) showed very similar UV absorptions and ^1H NMR resonances, the only difference being the additional signals of an O-isoprenyl chain in the former (see Exp.). The chain was easily lost (68 mu) from M^+ in the mass spectrum of 9 and the following fragmentation was coincident with that one of vismione E. Therefore the new vismione was assigned the structure 9 and the name of 6-O-prenylvismione E.

The known isolated anthranoids are described in the Experimental part.

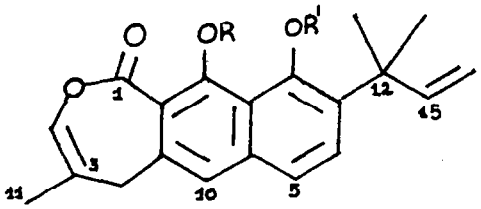
EXPERIMENTAL

The spectra were run with the following instruments: ^1H NMR, Varian EM 360; ^{13}C NMR, Varian XL 300; IR, Perkin Elmer 247; UV, Perkin Elmer Lambda 5; MS, AEI 14. Chromatography was on silica gel from Merck.

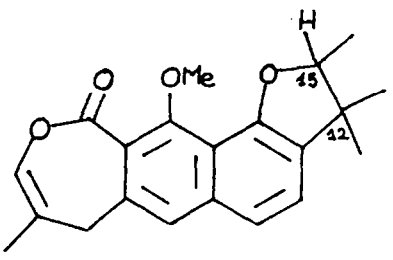
Plant material. The berries of Psorospermum glaberrimum were collected in Ivory Coast and identified by Dr. H. Téhé (ORSTOM, Adiopodoumé, Ivory Coast) and Dr. P. Garnier (Aubagne, France). A voucher sample is deposited in the Herbarium of Centro Chimica dei Recettori under the cypher PG 1986.

Extraction and separation. The ground berries (800 g) were extracted with cold Me_2CO exhaustively, to give a residue of 53 g. A portion (24 g) was parted between hexane and MeOH-H_2O, 9-1. The residue of the pooled hexane extracts on silica gel with CH_2Cl_2 gave the following products, which were purified by extended chromatography and crystallization: madagascin[9] (18 mg, mp 155-6°), homoferruginin B (6, 57 mg), 2-prenylphyscion anthrone (7, 30 mg), 3-O-geranyloxychrysophanol anthrone[10] (35 mg,mp 98-99°), psorolactone A (1, 3.1 g), physcion (32 mg, mp 210-1°), acetyltorosachrysone (8, 27 mg),acetylvismione F[11] (95 mg, mp 118-9°), vismione C[7] (65 mg, mp 100-4°), vismione D[7] (72 mg, mp 142-5°), psorolactone B (5, 115 mg), 2-geranylemodin[12] (35 mg, mp 207-9°), 2-prenylemodin[13] (64 mg, mp 240-2°), 6-O-prenylvismione E (9, 56 mg), vismione E[7] (70 mg, mp 161-3°) and vismione F[10] (300 mg, mp 144-6°).

The known compounds were identified by comparison with authentic samples.



	R	R'
1	H	H
1a	Me	H
1b	Me	Me
1c	COMe	COMe



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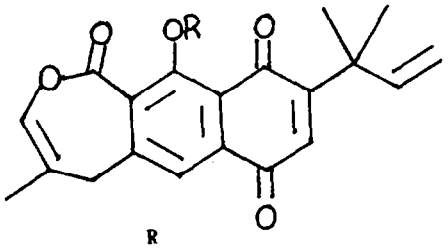
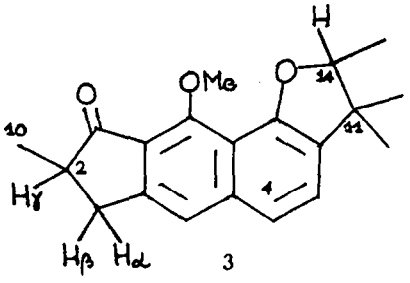


	R
5	H
5a	Me



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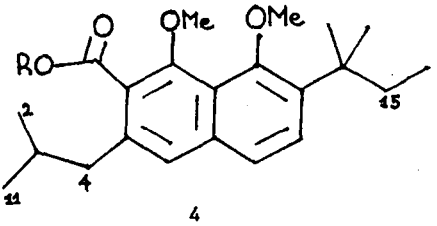

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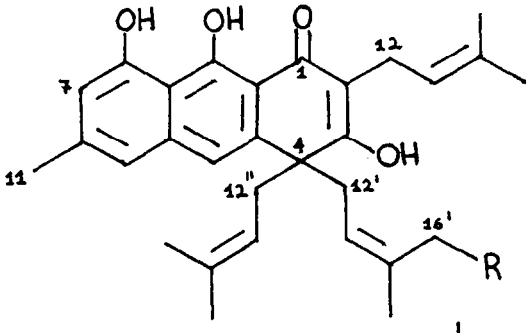
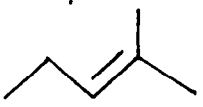
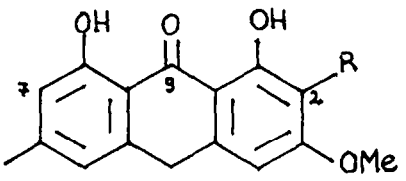
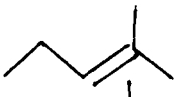
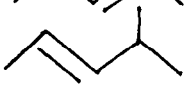
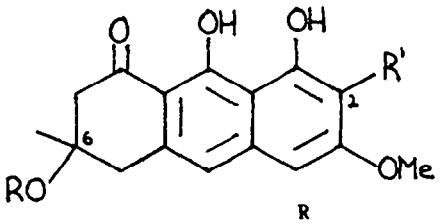


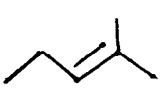
	R	=	
6	R	=	
6a	R	=	H

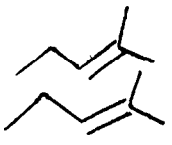


	R	=	
7	R	=	
7a	R	=	



	R	R'
8	COMe	H
8a	H	H

9	
9a	H



Psorolactone A (1). $C_{20}H_{20}O_4$; found 324.1368, calcd 324,1361). Vitreous solid; UV, IR and NMR data have been already reported [2]; EIMS m/z (rel. int.):324 (M^+, 100), 309 (62), 296 (20), 295 (20), 281 (45), 263 (58).

9-O-methylpsorolactone A (1a). To 1 (100 mg) in Et_2O a satd soln of CH_2N_2 in Et_2O was added. After 30' the solvent was evaporated to yield 9-O-methylpsorolactone A (1a, 113 mg); $C_{21}H_{22}O_4$ (M^+ 338), oil; IR ($CHCl_3$): 3320, 1720, 1620, 1565, 1350, 995, 910 cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.99 (1H,s,8-OH), 7.50 (1H,d,J= 8.5Hz,H-5), 7.12 (1H,d,J= 8.5Hz,H-6), 7.12 (1H,br s,H-10),6.2-5.9 (2H, m,H-2,H-15), 5.1-4.9 (2H,m,H_2-16), 3.94 (3H,s,9-OMe), 3.27 (2H,br s,H_2-4), 1.80 (3H,d,J= 0.3Hz,11-Me), 1.60 (6H,s,13-Me,14-Me); ^{13}C NMR: δ 165.0 (s,C-1), 159.2 (s,C-9), 153.0 (s,C-8), 147.7 (d,C-15), 139.1 (s,C-4a), 135.6 (s,C-10a), 134.1 (d,C-2), 129.5 (d,C-6), 129.9, 128.6 (2xd,C-3,C-7), 119.9 (d,C-10), 117.3 (d, C-5), 116.8 (s,C-9a), 109.9 (t,C-16), 109.7 (s,C-8a), 63.4 (q,9-OMe), 40.6 (s, C-12), 35.8 (t,C-4), 27.0 (q,13-Me, 14-Me), 17.4 (q,11-Me).

8,9-O-dimethylpsorolactone A (1b). 1 (300 mg), K_2CO_3 (700 mg) and Me_2SO_4 (5 ml) were held at reflux in dry acetone (25 ml) for 4 hr. Work up and purification on silica gel (CH_2Cl_2-hexane, 85-15) gave 8,9-O-dimethylpsorolactone(1b, 160 mg); $C_{22}H_{24}O_4$ (M^+ 352), mp 107-8°; IR ($CHCl_3$) ν_{max}: 1720, 1615, 1550, 980, 910, cm^{-1}; ^1H NMR ($CDCl_3$):δ 7.56 (1H,d,J= 8.5Hz,H-6), 7.47 (1H,d,J= 8.5Hz,H-5), 7.20 (1H,br s,H-10), 6.2-5.9 (2H,m,H-2,H-15), 5.1-4.9 (2H,m,H_2-16), 3.94 (3H,s, 9-OMe), 3.76 (3H,s,1-OMe), 3.66 (2H,brs,H_2-4), 1.80 (3H,d,J= 0.3Hz,11-OMe), 1.53 (6H,s,13-Me,14-Me);^{13}C NMR ($CDCl_3$): δ 164.7 (s,C-1), 157.7 (s,C-9), 155.5 (s,C-8), 148.9 (d,C-15), 139.6 (s,C-4a), 138.2 (s,C-10a), 137.0 (s,C-7), 134.6 (d,C-2), 128.7 (d,C-6), 127.6 (s,C-3), 122.7 (d,C-5), 121.4, 121.1 (2xs,C-8a, C-9a), 119.7 (d,C-10), 109.7 (t,C-16), 64.2, 63.2 (2xq,2xOMe), 41.1 (s, C-12), 35.5 (t,C-4), 28.6 (2xq,13-Me,14-Me), 17.8 (q, 11-Me);

8,9-O-Diacetylpsorolactone A (1c). Acetylation of 1 (110 mg) with pyr/Ac_2O at r.t. overnight afforded 8,9-O-diacetylpsorolactone A (1c, 122 mg); $C_{24}H_{24}O_6$, (M^+ 408), mp 155-6°; ^1H NMR ($CDCl_3$): δ 2.34, 2.26 (2x3H, 2xs, 2xCOMe).

Treatment with acids. a) with AcOH: 9-O-methylpsorolactone (1a, 70 mg) was left overnight in AcOH (2 ml) and MeOH (6 ml). After elimination of the solvent, compound 1a was recovered unchanged (68 mg).

b) with TFA: To 1a (105 mg) a soln $CHCl_3$-TFA, 7-3 (10 ml) was added and the mixture was left standing overnight. The residue of the reaction mixture on silica gel with CH_2Cl_2 yielded compounds 2 (50 mg) and 3 (45 mg).

When the mixture was left standing for 48 hr only 3 (87 mg) was obtained.

c) with H_2SO_4: 1a (100 mg) and conc H_2SO_4 (3 ml) in MeOH (9 ml) were left standing overnight.Standard work up gave compound 3 (62 mg) as the main product.

Compound 2. $C_{21}H_{22}O_4$ (M^+ 338), oil; UV (MeOH) λ_{max}: 252, 286sh, 318sh, 362 nm (logε 4.60, 4.00, 3.59, 3.62); IR ($CHCl_3$) ν_{max}: 1720, 1628, 1560, 1370, 1170 cm^{-1}; ^1H NMR and ^{13}C NMR spectra in ref.2.

Compound 3. Mp 115-7°, $C_{20}H_{22}O_3$; found 310.1537, calcd 310.1569; UV (MeOH) λ_{max}: 265, 297, 309, 398 nm (logε 4.70, 3.66, 3.63, 3.73); IR ($CHCl_3$) ν_{max}: 1700, 1620, 1570, 1370, 1070 cm^{-1}; ^1H NMR ($CDCl_3$): δ (1H,s,H-9), 7.23 (2H,s, H-4,H-5), 4.55 (1H,q,J= 6.5Hz,H-14), 4.00 (3H,s,9-OMe), 3.30 (1H,dd,J= 17 and 3.5Hz, H-α), 2.70 (1H,dd,J= 17 and 9Hz,H-β), 2.55 (1H,m,H-γ),1.45 (3H,d,J= 6.5Hz,15-Me), 1.33, 1.13 (2x3H,2xs,12-Me,13-Me), 1.27 (3H,d,J= 6.5Hz,10-Me); ^{13}C NMR ($CDCl_3$): δ 206.0 (s, C-1), 156.5, 155.6 (2xs,C-7,C-8), 146.3 (s,C-3a), 139.9 (s,C-9a), 131.7 (s,C-6), 124.0 (d,C-5), 119.8, 119.4 (2xd,C-4,C-9), 119.5 (s,C-8a), 115.8 (s,C-7a), 89.7 (d,C-14), 63.1 (q,9-OMe), 43.2 (s,C-11),43.1 (d, C-2), 34.1 (t,C-3), 26.8, 22.9 (2xq,C-12,C-13), 16.3 (q,C-10), 14.7 (q,C-15); EIMS m/z (rel. int.): 310 (M^+, 68), 295 (100), 239 (50).

Hydrogenation. 8,9-O-dimethylpsorolactone (1b, 100 mg) in AcOH was reacted with H_2/PtO_2 overnight.The residue of the filtered reaction mixture was treated with a satd soln of CH_2N_2 in Et_2O to give after purification (silica gel,CH_2Cl_2) compound 4 (R=Me, 24 mg); oil, $C_{23}H_{32}O_4$; UV (MeOH) λ_{max}: 255, 265sh, 353 nm (logε 4.17, 3.98, 3.58); IR ($CHCl_3$) ν_{max}: 1730, 1660, 1590 cm^{-1}; ^1H and ^{13}C NMR data have been reported in ref. 2; EIMS m/z (rel. int.): 372 (M^+, 38) 341 (31), 340 (38), 325 (22), 307 (100).

Psorolactone B (5). Mp 217-8°,$C_{20}H_{18}O_5$;found 338.1143, calcd 338.1154;UV (MeOH) λ_{max}: 226, 263, 282sh, 420 nm (logε 4.20, 3.82, 3.75, 3.50);(+MeONa): 274, 539; (+$AlCl_3$ and + $AlCl_3$/HCl): 227, 262, 308, 362, 506; IR ($CHCl_3$) ν_{max}: 1730, 1665, 1635, 1600, 1570, 1360, 1135, 915 cm^{-1}; ^1H NMR (CCl_4):δ 12.63 (1H,s,9-OH), 7.18 (1H,br s,H-10), 6.73 (1H,s,H-6), 6.2-5.9 (2H,m,H-2,H-15), 5.1-4.9 (2H,m,H_2-16), 3.27 (2H,br s, H_2-4), 1.80 (3H,d,J= 0.3Hz, 11-Me), 1.47 (6H,s,13-Me, 14-Me); ^{13}C NMR ($CDCl_3$): δ 189.8 (s,C-8), 184.4 (s,C-5), 162.1 (s,C-1), 157.3 (s,C-9), 152.9 (s,C-7),145.0 (d,C-15), 140.8 (s,C-4a), 135.6, 134.8 (2xd,C-2,C-6),132.9 (s,C-10a), 127.0 (s,C-3), 122.8 (s,C-9a), 115.2 (d,C-10), 113.4 (t,C-16), 111.6 (s,C-8a), 41.1 (s,C-12), 36.2 (t,C-4), 27.2 (q,C-13,C-14), 18.0 (q,C-11); EIMS m/z (rel. int.): 338 (M^+, 100), 323 (23), 309 (19), 295 (34),277 (23),267 (20).

9-O-methylpsorolactone B (5a). To psorolactone B (80 mg) and K_2CO_3 (800 mg) in dry Me_2CO (20 ml) was added Me_2SO_4 (1 ml) and the mixture was held at reflux for 6 hr. Standard work up and purification on silica gel with C_6H_6 gave 9-O-methylpsorolactone B (5a, 30 mg); oil, $C_{21}H_{20}O_5$; UV (MeOH) λ_{max}: 226, 261, 420 nm (logε 4.15, 3.73, 3.20); ^1H NMR ($CDCl_3$):δ 7.60 (1H,br s,H-10), 6.83 (1H, s,H-6), 6.2-5.9 (2H,m,H-2,H-15), 5.1-4.9 (2H,m,H_2-16), 3.95 (3H,s,9-OMe), 3.33 (2H,br s,H_2-4), 1.80 (3H,d,J= 0.3 Hz,11-Me), 1.45 (6H,s,13-Me,14-Me); ^{13}C NMR ($CDCl_3$): δ 184.9 (s,C-8), 183.1 (s,C-5), 162.6 (s,C-1), 159.4 (s, C-9), 150.3 (s,C-7), 145.4 (d,C-15), 139.0 (s,C-4a), 135.3 (d,C-2), 134.7 (s,C-10a), 132.4 (d,C-6), 118.6 (d,C-10), 117.0 (s,C-8a), 116.3 (s,C-9a), 112.9 (t,C-16), 127.5 (s,C-3), 64.7 (q,OMe), 41.3 (s,C-12), 35.6 (t,C-4), 27.2 (q,13-Me,14-Me), 18.0 (q,11-Me); EIMS m/z (rel. int.): 352 (M^+, 100), 337 (20), 309 (50), 281 (32).

Oxidation of 9-O-methylpsorolactone A to 9-O-methylpsorolactone B. To a soln of 1a (100 mg) in CH_2Cl_2 (20 ml) at 0° was added the TTN/celite (234 mg/632 mg) reagent[3]. The mixture was stirred 2 hr and filtered. The residue (silica gel, C_6H_6) afforded compound 5a (55 mg), identical with the methyl derivative of 5.

Homoferruginin B (6). Oil, $C_{30}H_{36}O_4$; UV ($CHCl_3$) λ_{max}: 242, 321, 414 nm; IR ($CHCl_3$) ν_{max}: 3350, 1630, 1600, 1580 cm^{-1}; ^1H NMR ($CDCl_3$): δ 17.10 (1H,s,exchg D_2O),9-OH), 9.99 (1H,s,exchg D_2O,8-OH), 7.08, 6.93 (1H each,br s,H-5,H-10), 6.63 (1H,br s,H-7), 5.10, 4.80 (1H each,br t,J= 7Hz,2x =CH), 4.55 (2H,br t,J= 7Hz,2x =CH), 3.26, 2.87, 2.60 (2H each,d,J= 7Hz,3x CH_2), 2.40 (3H,s,6-Me), 1.78 (10H,br s,2x CH_2, 2xMe), 1.56 (3H,br s,Me), 1.42 (12H,br s,4xMe); ^{13}C NMR ($CDCl_3$): δ 193.8 (s,C-1), 181.1 (s,C-3), 163.2 (s,C-9), 157.2 (s,C-8), 141.8 (s,C-4a), 140.0 (d,C-6), 138.3, 138.2 (2xs,C-14',C-14"), 137.7 (s,C-5a), 134.8 (s,C-14), 131.8 (s,C-19'), 123.8 (d,C-18'), 121.1 (d,C-5), 118.8, 118.3 (2xs, C-1a,C-2), 118.6, 118.5, 117.8 (3xd,C-13,C-13',C-13"), 114.7 (d,C-10), 111.6 (d,C-7), 111.0 (s,C-8a), 49.4 (s,C-4), 40.8, 40.3 (2xt,C-12', C-12"), 39.7 (t, C-16'), 26.6 (q,C-17'), 25.8, 25.7, 25.5 (3xq,C-15,C-20',C-15"), 22.1 (t,C-12), 20.9 (q,C-11), 18.0, 17.9, 17.5 (3xq,C-16,C-21',C-16"), 16.3 (q,C-15'); EIMS m/z (rel. int.): 528 (M^+, 13), 485 (3), 473 (M - C_4H_7, 8), 472 (9), 460 (18), 459 (26), 404 (43), 403 (35), 392 (M - $C_{10}H_{16}$, 52), 391 (59), 337 (55), 349 (35), 337 (55), 336 (392 - C_4H_8, 84), 335 (81), 293 (92), 281 (66), 280 (336 - C_4H_8, 100); m^* 423.7 (528 → 473), 291.0 (528 → 392), 288.0 (392 → 336), 233.3 (336 → 280).

2-Prenylphyscion anthrone (7). Mp 191-2°, $C_{21}H_{22}O_4$; UV ($CHCl_3$) λ_{max}: 270, 350 nm (log ε 4.70, 4.48); ^1H NMR ($CDCl_3$): δ 12.06, 11.90 (1H each,s,exchg D_2O,1-OH, 8-OH), 6.70, 6.65 (1H each, br s, H-5, H-7), 6.43 (1H, br s, H-7), 5.33 (1H, br t,J= 7.5Hz,=CH), 4.26 (2H,s,H2-10), 3.99 (3H,s,OMe), 3.40 (2H,d,J= 7.5Hz,CH2), 2.43 (3H,s,6-Me), 1.90, 1.76 (3H each,br s,2xMe); EIMS m/z (rel. int.): 338 (M^+, 50), 323 (28), 295 (M - C_3H_7, 100), 283 (M - C_4H_7, 90); m* 257.5 (338 → 295), 236.9 (338 → 283).

Acetyltorosachrysone (8). Mp 157-9°, $C_{18}H_8O_6$; UV (MeOH) λ_{max}:273, 316sh, 330sh, 400 nm (log ε 4.68, 3.90, 3.76, 4.14); ^1H NMR ($CDCl_3$): δ 16.00 (1H,s,exchg D_2O, 8-OH), 9.53 (1H,s,exchg D_2O,1-OH), 6.78 (1H,s,H-10), 6.52 (1H,d,J= 2Hz,H-4), 6.32 (1H,d,J= 2Hz,H-2), 3.78 (3H,s,OMe), 3.72, 3.50 (1H each,d,J= 16Hz,5-CH_2), 3.1-2.7 (2H,m,7-CH_2), 1.83 (3H,s,COMe), 1.66 (3H,s,6-Me); EIMS m/z (rel. int.): 330 (M^+, 10), 270 (M - AcOH, 100), 255 (28), 242 (12), 241 (13), 227 (38); m* 240.8 (270 → 255), 216.9 (270 → 242), 212.9 (242 → 227), 202.1 (255 → 227).

6-O-Prenylvismione E (9). Oil, $C_{26}H_{32}O_5$; UV (MeOH) λ_{max}: 230, 280, 320, 400 nm; ^1H NMR ($CDCl_3$): δ 16.0 (1H,br s,exchg D_2O,9-OH), 9.77 (1H,s, exchg D_2O,1-OH), 6.66 (1H,s,H-10), 6.37 (1H,s,H-4), 5.20 (2H,br t,J= 7.5Hz,2x=CH), 4.55 (2H,d,J= 7.5Hz,OCH_2), 3.81 (3H,s,OMe), 3.37 (2H,d,J= 7.5Hz,CH_2), 2.93 (2H,br s,5-CH_2), 2.73 (2H,br s,7-CH_2), 1.8-1.7 (12H,4xMe), 1.37 (3H,s,6-Me); ^{13}C NMR:δ 201.6 (s, C-8), 166.3 (s,C-9), 162.3 (s,C-1), 155.7 (s,C-3), 141.2,139.2 (2xs,C-5a,C-20), 135.1, 134.4 (2xs,C-4a,C-14), 124.5, 122.1 (2xs,C-13,C-19), 117.6 (d,C-10), 108.0 (s,C-8a), 101.5, 100.8 (2xs,C-2,C-9a), 97.8 (d,C-4), 71.0 (s,C-6), 65.1 (t,C-18), 55.5 (q, C-17), 43.3 (t,C-5), 28.9 (s,C-11), 26.7, 26.3 (2xq,C-15, C-21), 25.6 (t,C-12), 17.7,16.1 (2xq,C-16,C-22); EIMS m/z (rel. int.): 424 (M^+, 27), 356 (M - C_5H_8, 82), 341 (36), 313 (14), 301 (356 - C_4H_7, 100), 295 (18).

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