Bull.Chem.Soc.Ethiop.1,(1), 42-46(1987).

NEW VISMIONES FROM *PSOROSPERMUM TENUIFOLIUM**

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(Received May 21, 1987)

ABSTRACT: Re-examination of the MeOH soluble portion of the acetone extract from root bark of *Psorospermum tenuifolium* afforded three new vismiones and a new C-alkylated emodin.

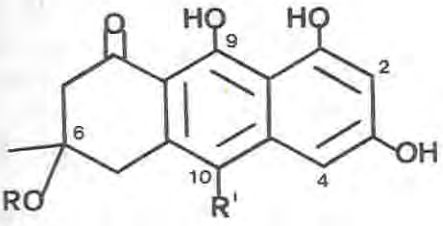
INTRODUCTION

In our systematic study of the tribe Vismieae (fam. Guttiferae, subfam. Hypericoideae), we have isolated several geranylated and prenylated anthranoids from the cold acetone extract of the root bark of *Psorospermum tenuifolium* (1). We have now re-examined the MeOH soluble fraction of the extract, after removal of the hexane soluble components. This paper deals with the isolation and structure elucidation of three new vismiones and 2-(18,19-dihydro-19-hydroxygeranyl)-6-methyl-1,8-dihydroxyanthraquinone. Two of the new vismiones obtained are the deacetylderivatives of previously isolated vismiones, namely vismione G 2a (2) and vismione H 3a (3).

RESULTS AND DISCUSSION

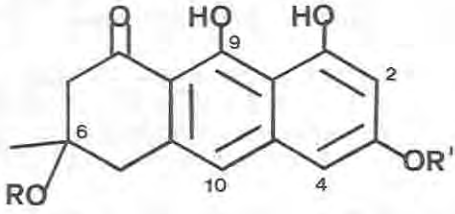
In addition to metabolites reported in our previous paper (1), 2-geranylemodin (4) and the corresponding 9-anthrone (2) were isolated from the MeOH soluble portion. These are the transformation products of acetylvismione F and vismione F, also present in the plant extract (1). The same relationship links 2-isoprenylemodin (5) and vismione C (6), which were now isolated together. Two of the new pigments, $C_{22}H_{24}O_6$, **1**, and $C_{25}H_{30}O_5$, **2** showed the same UV chromophore and the same aromatic substitution pattern in the ^1H NMR spectra as compared with compound, 2a (2), $C_{27}H_{32}O_6$. Both **1** and 2a have a 6-O-acetyl group (7), confirmed by the loss of 60 mu from M^+ in the mass spectrum, and differ in the C-10 substituents, the geranyl chain of 2a being replaced by a prenyl chain in **1** (^1H NMR evidence). As it was noted for 2a (2) and now confirmed for **1**, in the mass spectrum the alkyl chain is lost in the typical way of an aliphatic substituent ($C_{10}H_{16}$ and C_5H_8, respectively), as a consequence of the rearrangement to anthrone of the ion $M - HOAc^+$. To the new vismione the structure **1** and the name acetylvismione K were thus assigned. The ^1H NMR spectrum of compound **2** displayed the presence of a C-10 geranyl chain as in 2a, but also the typical signals of a 6-hydroxyvismione (7).

Accordingly the mass fragmentation of 2, after the loss of H_2O from M^+, was coincident with that of 2a, after the loss of HOAC (2), and structure 2 and the name deacetylvismione G were derived for the new product.



	R	R'
1	$COCH_3$	Prenyl
2	H	Geranyl
2	$COCH_3$	Geranyl

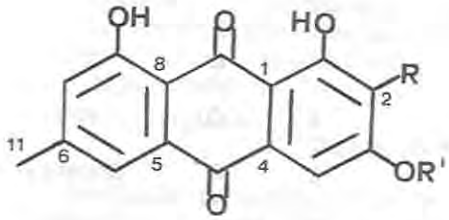
The substitution pattern of the third vismione, $C_{20}H_{22}O_5$ **3**, could be related to those of vismione H 3a and vismione D 3b (4); examination of the ^1H NMR spectrum showed compound 3 to have a 3-O-prenyl chain as the former and a 6-OH group as the latter. In the mass fragmentation the losses of H_2O and C_5H_8 from M^+ afforded the same base peak (at m/z 256) which was displayed by 3a (3), after the losses of AcOH and C_5H_8, and by 3b (5), after the losses of H_2O and $C_{10}H_{16}$. The above considerations led to structure 3 and the name deacetylvismione H for the third compound.



	R	R'
3	H	Prenyl
3a	$COCH_3$	Prenyl
3b	H	Geranyl
3c	$COCH_3$	Geranyl

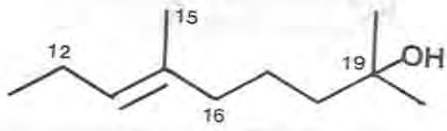
If we consider the couples 2a and **1**, 3b and 3, acetylvismione D 3c (1,8) and 3a, as well as acetylvismione F (1,2) and vismione C (6), we may conclude that the extract of *Psorospermum tenuifolium* is characterized by the co-occurrence of the more abundant typical (7) geranylated vismiones and the corresponding prenylated analogous ones. UV and ^1H NMR data (see Experimental Part) of a fourth pigment, $C_{25}H_{28}O_6$ 4, optically inactive, resembled those of 2-geranylemodin (4). The nature of the substituent was established by comparison with the isomer 4a (1,9), particularly by the coincidence of the C-13 to C-21 signals in the ^{13}C NMR spectrum. Consequently,

the structure of 2-(18,19-dihydro-19-hydroxygeranyl)-6-methyl-1,3,8-trihydroxyanthraquinone 4 was attributed to the metabolite.



	R	R'
4	Z	H
4a	H	Z

Z =



EXPERIMENTAL

General: Mps were determined with a Kofler apparatus and are uncorrected. Spectra were recorded with the following instruments: ^{1}H NMR, Varian EM 360; ^{13}C NMR, XL 300; UV, Perkin Elmer Lambda 5; MS, AEI 14.

Extraction and fractionation:- A portion (15 g) of the cold acetone extract of *Psorospermum tenuifolium* (1) was dissolved in 300 ml of MeOH-H_2O, 93:7, and the soln was washed with hexane (5x250 ml). The residue of the pooled hexane extracts (9.5 g) showed on tlc the same components isolated and reported in our previous paper (1) and was discarded.

The MeOH residue (5.5 g) on silica gel with CH_2Cl_2 - EtOAc, 4:1, gave eight fractions PTM1 - PTM8, which on further purification yeilded: acetylvismione D (1,8), 2-geranylemodinanthrone (2) (150 mg, mp 153-5°C), acetylvismione F (1,2), 2-geranylemodin (4) (25 mg, mp 207-9°C), vismione G (2) (2a, 20 mg, mp 184-7°C), vismione C (6) (10 mg, mp 100-5°C), 2-isoprenylemodin (4) (15 mg, mp 240-2°C) and emodin from PTM1 (silica gel; hexane-EtOAc, 3:1, and plc); vismione H (1,3) (3a), acetylvismione F, vismione C (10 mg), vismione G (30 mg), acetylvismione K (1,10 mg) and emodin from PTM2 (silica gel; $CHCl_3$-MeOH, 199:1, and plc); emodin and 3-(18,19-dihydro-19-hydroxy-geranyloxy)-6-methyl-1,8-dihydroxyanthraquinone (1,7) from PTM3 (silica gel; hexane-EtOAc, 3:2); vismione D (1,4), 1,3,8,10-tetrahydroxy-6-methyl-10-prenylanthrone (1) and deacetylvismione G (2, 13 mg) from PTM4 (silica gel; $CHCl_3$-MeOH, 32:1, and plc); vismione D from PTM5; vismione D, deacetylvismione H (3, 40 mg and 2-(18,19-dihydro-19-hydroxygeranyl)-6-methyl-1,8-dihydroxyanthraquinone (4,60 mg) from PTM6 (silica gel; $CHCl_3$ - MeOH, 32:1, and plc); vismione F (6) from PTM7; 3-(18,19-dihydro-18,19-dihydroxygeranyloxy)-6-methyl-1,8-dihydroxyanthraquinone (1) from PTM8.

New compounds: Acetylvismione K (1). $C_{22}H_{24}O_6$, mp 109-10°C (Et_2O); M^+ calc., 384.1573; found, 384.1571; UV λ_{max} ($CHCl_3$) nm (log ε): 278 (4.30), 320 (3.63), 333sh (3.54), 400 (3.67); λ_{max} (MeOH): 273, 318, 326sh, 396; λ_{max} (NaOAc): 275, 402; ^{1}H NMR (Me_2CO-d_6): δ 16.85 (1H, br s, 9-OH), 10.15 (1H, br s, 1-OH), 9.20 (1H, br s, 3-OH), 6.79 (1H,d, J = 2Hz, H-4), 6.43 (1H, d, J = 2Hz, H-2), 5.01 (1H,m, = CH), 3.62, 3.31 (1H each, q, J = 16Hz, 5-CH_2), 3.47 (2H, br d, J = 7Hz, CH_2), 3.16 (2H, br s, 7-CH_2), 1.89, 1.79 (3H each, br s, 2xMe), 1.81 (3H, s, COMe), 1.74 (3H, s, 6-Me); EIMS (probe) 70eV, m/z (rel. int.) : 384 M^+ (3), 324 [M - HOAc]$^+$ (12), 270 (20), 268 [324 - C_4H_8]$^+$ (24), 256 [324 - C_5H_8]$^+$ (100), 255 (50), 227 (20), 69 (25), 41 (15); m* 221.7 (324 → 268), 202.3 (324→ 256), 24.4 (69 → 41).

Deacetylvismione G (2). $C_{25}H_{30}O_5$, vitreous solid; M^+ calc. 410.2093; found, 410.2107; UV λ_{max} ($CHCl_3$) nm (log ε): 278 (4.25), 321 (3.55), 404 (3.62); λ_{max} (MeOH): 272, 316, 394; λ_{max} (NaOAc): 274, 401; ^{1}NMR (Me_2CO-d_6): δ 16.98 (1H, s, 9-OH), 10.20 (1H, s, 1-OH), 9.15 (1H, br s, 3-OH), 6.75 (1H, d, J = 2Hz, H-4), 6.39 (1H, d, J = 2Hz, H-2), 5.30 (1H, br t, J =7Hz, =CH), 5.00 (1H, m, = CH), 3.48 (2H, d, J = 7Hz, CH_2), 3.07 (2H each, br s, 5-CH_2, 7-CH_2), 2.4 2.1 (4H,m, 2xCH_2), 1.68 (9H, br s, 3xMe), 1.40 (3H, s, 6-Me); EIMS 70eV (probe) m/z (rel. Int.): 410 M^+ (11), 392 [M - H_2O]$^+$ (3), 270 [392 -C_9H_{14}]$^+$ (73), 256 [392 - $C_{10}H_{14}$]$^+$, 227 (26), 137 [$C_{10}H_{17}$]$^+$ (100), 135 (75).

Deacetylvismione H (3). $C_{20}H_{22}O_5$, M^+ calc., 342.1467; found, 342.1473; mp 155-6°C (Et_2O); λ_{max} ($CHCl_3$) nm (log ε): 277 (4.71), 320 (3.96), 332sh (3.86), 394 (4.16); ^{1}H NMR (Me_2CO-d_6): δ16.30 (1H, br s, 9-OH), 9.69 (1H, s, 1-OH), 6.88 (1H, br s, H-5), 6.65(1H, d, J = 2Hz, H-4), 6.36 (1H d, J = 2Hz, H-2), 5.48 (1H, br t, J = 7Hz, = CH), 4.60 (2H, d, J = 7Hz, CH_2), 3.06, 2.83 (2H each, br s, 5-CH_2, 7-CH_2), 1.82 (6H, br s, 2xMe), 1,45 (3H, s, 6-Me); EI MS 70 eV (probe) m/z (rel. int.): 342 M^+ (20), 324 [M - H_2O]$^+$ (13), 274 [M-C_5H_8]$^+$ (87), 256 [324 - C_5H_8 and 274 - H_2O]$^+$ (100), 241 (7), 227 (8), 69 (40), 41 (25); m* 239.2 (274 → 256), 219.5 (342 →274), 202.3 (324 → 256), 24.4 (69 → 41).

2-(18,19-dihydro-19-hydroxygeranyl)-6-methyl-1,3,8-trihydroxyanthraquinone (4). $C_{25}H_{28}O_6$, M^+ calc., 424.1886; found, 424.1884; mp 200-1°C (Et_2O); UV λ_{max} (EtOH) nm (log ε): 283 (4.71),438 (4.36); λ_{max} (NaOAc): 257, 325, 438, 518; λ_{max} ($AlCl_3$): 276, 311, 363, 496, 522sh (after 20'); ^{1}H NMR ($CDCl_3$): 12.50, 12.12 (1H each, s, 1-OH, 8-OH), 7.50 (1H, br s, H-5), 7.27 (1H, s, H-4), 7.0 (1H, br s, H-7), 5.3 (1H, m, = CH), 3.42 (2H, d, J = 7Hz, CH_2), 2.40 (3H, br s, 6-Me), 2.3 - 2.0 (2H, m, CH_2), 1.78 (3H, br s, Me), 1.7 - 1.3 (4H, m, 2xCH_2), 1.17 (6H, s, 2xMe); ^{13}C NMR ($CDCl_3$): δ 191.0 (C-9), 182.1 (C-10), 163.0, 162.5, 161.9 (C-1, C-3, C-8), 148.3 (C-6), 142.0 (C-14), 136.6 (C-5a), 133.2 (C-4a), 124.5 (C-7), 121.1 (C-13), 120.2 (C-5), 110.0 (C-1a), 106.1 (C-2), 70.5 (C-19), 43.1 (C-18), 39.9 (C-16), 29.7, 29.2(C-20, C-21), 22.4, 22.1, 22.0 (C-11, C-12, C-17), 16.3 (C-15); EIMS 70eV (probe) m/z (rel.int.): 424 M^+ (5), 406 [M-H_2O]$^+$ (17), 391 [406-Me]$^+$ (3), 363 [406-C_3H_7]$^+$

(9), 350 [406-C_4H_8]$^+$ 337 [406-C_5H_9]$^+$ (26), 335 (23) 323 (18), 321 [406 -C_6H_{13}]$^+$ (60), 309 (13), 295 (53), 284 (88), 283 [M-$C_9H_{17}O$]$^+$ (100), 270 (25), 256 (14), 123 [C_9H_{15}]$^+$ (38).

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* Part 6 in the series: "Chemistry of the *Psorospermum* genus". For part 5 see ref (1).

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