

A NOVEL TYPE OF PRENYLATED ANTHRANOID FROM PSOROSPERMUM GLABERRIMUM

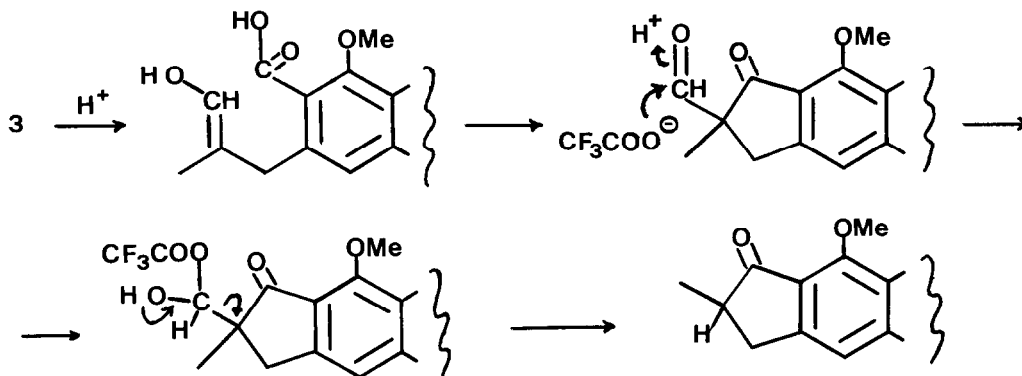
Bruno Botta, Franco Delle Monache\*, and Giuliano Delle Monache  
Centro Chimica dei Recettori, Istituto di Chimica, Università  
Cattolica S. Cuore, Largo F. Vito 1, 00168 Roma, Italy

Abstract: Psorolactone, belonging to a new class of prenylated anthranoids, has been isolated from Psorospermum glaberrimum and its structure determined on the basis of the spectral data and chemical transformations.

During our chemosystematic investigation of South American Vismia spp and African Psorospermum spp (Vismieae) several biologically active vismiones and ferruginins [1] have been isolated. These prenylated anthranoids (a representative of each class is shown in 1 and 2) are characterized by a non aromatic ring A or C, respectively.

From the berries of Psorospermum glaberrimum, collected in the Ivory Coast, we have now isolated a new type of prenylated anthranoid containing a lactone A ring. Chromatography of the acetone extract afforded inter alia a compound  $C_{20}H_{20}O_4$ , named psorolactone, 3, which contained a 1,8-dihydroxynaphthalene moiety, but exhibited spectral features ( $\lambda_{max}^{MeOH}$  260, 304sh, 318, 391 nm;  $\nu_{max}^{CHCl_3}$  3380, 1655, 1630, 1570, 995, 910  $cm^{-1}$ ; NMR spectra in Table 1) quite different from those of vismiones and ferruginins [1]. In particular, the upfield shift ( $\delta$  13.7 vs 16.3 in 1 and 17.1 in 2 [1]) of the 9-OH in the  $^1H$  NMR spectrum suggested a different kind of chelation and since the alicyclic ring had to contain an extra oxygen, the presence of the lactone ring as depicted in 3 was postulated. By the presence of two ortho coupled aromatic protons, the  $\alpha, \alpha$ -dimethylallyl chain ( $^1H$  NMR evidence) could be located either on C-7 or C-5. The C-7 substitution was established when the monomethyl derivative 4 [2], obtained by treatment of 3 with  $CH_3N_2$ , was treated with TFA to yield compound 5,  $C_{21}H_{22}O_4$ , in which an  $\alpha, \alpha, \beta$ -trimethyldihydrofuran ring was present [3]. The above reaction gave one more product 6,  $C_{20}H_{22}O_3$ , in which the ring closure of the side chain

present in **3** had occurred, as well as a modification of the lactone ring. The latter compound now possessed signals in the NMR spectra characteristic of a 2-methylcyclopentanone ring ( $^1\text{H}$  NMR:  $\delta$  3.3, q,  $J=17$  and  $3.5\text{Hz}$ , H- $\alpha$ ; 2.7, q,  $J=17$  and  $9\text{Hz}$ , H- $\beta$ ; 2.55, m, H- $\gamma$ ; 1.27, d,  $J=6.5\text{Hz}$ , Me;  $^{13}\text{C}$  NMR:  $\delta$  206, CO; 43.1, C-2; 34.1, C-3; 16.3, Me). Compound **5** was converted into **6**, when the reaction mixture was allowed to stand for a longer time, and **6** was the main product when the reaction was carried out in  $\text{H}_2\text{SO}_4$ . Scheme 1 illustrates a plausible mechanism for the ring contraction proposed above.



Scheme 1

The postulated A ring was supported by  $\text{PtO}_2$  catalyzed hydrogenation in AcOH of the dimethyl derivative **7**,  $\text{C}_{22}\text{H}_{24}\text{O}_4$  (formed by reaction of **3** with  $\text{Me}_2\text{SO}$ ). The latter reaction afforded an acid, isolated as its methylester  $\text{C}_{23}\text{H}_{32}\text{O}_4$ , and formulated as **8** on the basis of the spectral data [4]. The formation of **8** may be explained through the hydrolytic A ring opening by AcOH and subsequent hydrogenation/hydrogenolysis. Biogenetically psorolactone **3** may derive from a vismione by a Baeyer-Villiger type oxidation.

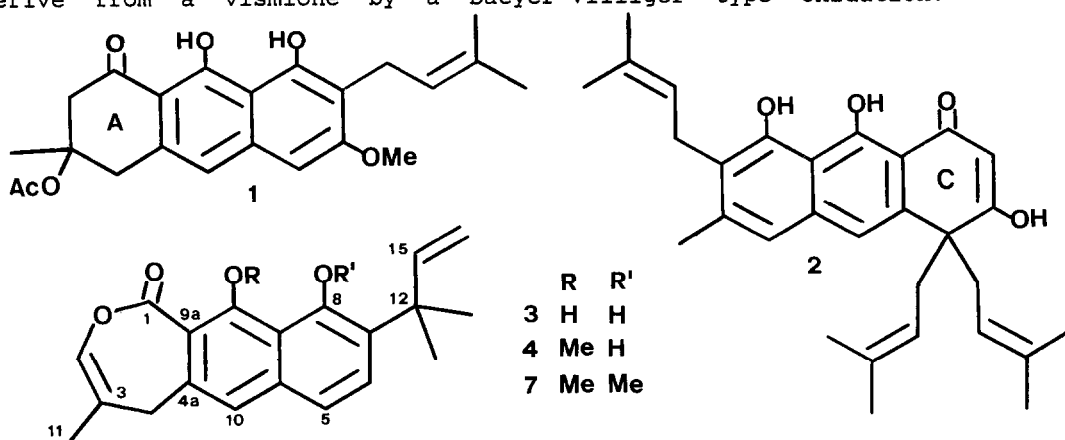


Table 1.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR data for 3

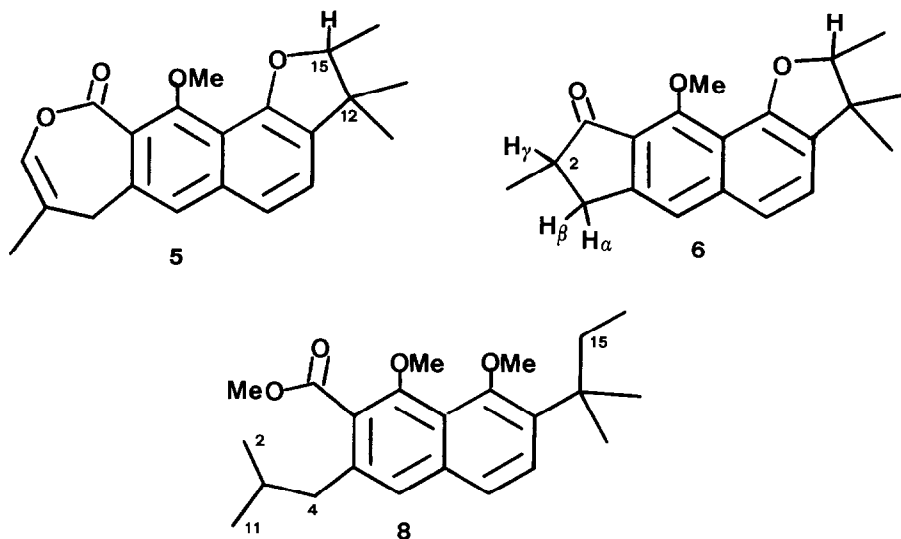
C/H Number	$\delta^a_{\text{C}}$	$\delta^b_{\text{H}}$
C-1	171.6	
C-2/H-2	135.1	6.27 m
C-3	128.8 <sup>c</sup>	
C-4/H <sub>2</sub> -4	36.7	3.40 br s
C-4a	135.2 <sup>d</sup>	
C-5/H-5	117.0 <sup>e</sup>	7.60 d (J 8.5Hz)
C-6/H-6	131.4	7.10 d (J 8.5Hz)
C-7	129.6 <sup>c</sup>	
C-8/OH-8	155.1	10.15 s
C-8a	104.1	
C-9/OH-9	164.4	13.68 s
C-9a	113.0	
C-10/H-10	117.1 <sup>e</sup>	6.90 br s <sup>f</sup>
C-10a	136.9 <sup>d</sup>	
C-11/Me-11	17.2	1.80 d (J 1.5Hz)
C-12	40.7	
C-13/Me-13	27.1	1.55 s
C-14/Me-14	27.1	1.55 s
C-15/H-15	147.8	6.30 m
C-16/H-16	110.1	5.0 m

a 75 MHz,  $\text{CDCl}_3$

b 300 MHz,  $\text{CDCl}_3$

c,d,e Assignments may be reversed

f Enhanced by irradiating at  $\delta$  3.40



#### Acknowledgment

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#### References and footnotes

- 1) F. Delle Monache, *Rev. Latinoamer. Quim.*, **16**, 5 (1985).
- 2) 4,  $^1\text{H NMR}$ :  $\delta$  10.0 (OH-10), 4.0 (OMe-9).
- 3) 5,  $\text{C}_{21}\text{H}_{22}\text{O}_4$ , found 338.1508, calcd 338.1518;  $^1\text{H NMR}$ :  $\delta$  7.23 (s, H-5, H-6), 7.13 (s, H-10), 6.05 (q,  $J=1.5\text{Hz}$ , H-2), 4.55 (q,  $J=6.5\text{Hz}$ , H-15), 4.0 (s, OMe-9), 3.26 (s,  $\text{H}_2$ -4), 1.70 (d,  $J=1.5\text{Hz}$ , Me-11), 1.42 (d,  $J=6.5\text{Hz}$ , Me-16), 1.33 and 1.13 (ss, Me-13, Me-14);  $^{13}\text{C NMR}$ :  $\delta$  163.1 (C-1), 157.9 (C-9), 153.6 (C-8), 139.2 (C-10a), 136.6 (C-4a), 134.4 (C-2), 132.6 (C-7), 127.5 (C-3), 123.6 (C-6), 121.0, 120.3 (C-8a, C-9a), 119.9, 119.4 (C-10, C-5), 89.8 (C-15), 64.6 (OMe), 43.5 (C-12), 35.8 (C-4), 26.7, 23.0 (C-13, C-14), 17.6 (C-11), 14.7 (C-16).
- 4) 8,  $\text{M}^{\text{I}}$  372;  $^1\text{H NMR}$ :  $\delta$  7.35 (s, H-5, H-6), 7.26 (s, H-10), 3.90, 3.77, 3.70 (ss, 3xOMe), 2.57 (d,  $J=6\text{Hz}$ ,  $\text{H}_2$ -4), 1.90 (q,  $J=6.5\text{Hz}$ ,  $\text{H}_2$ -15), 1.40 (s, Me-13, Me-14), 1.27 (m, H-3), 0.93 (d,  $J=6\text{Hz}$ , Me-2, Me-11), 0.70 (t,  $J=6.5\text{Hz}$ , Me-16);  $^{13}\text{C NMR}$ :  $\delta$  169.3 (C-1), 154.7, 152.6 (C-8, C-9), 137.0, 136.4, 135.4 (C-4a, C-7, C-10a), 127.9 (C-6), 126.9 (C-6a), 124.6 (C-10), 122.8 (C-5), 119.7 (C-8a), 67.6, 60.6 (OMe-8, OMe-9), 52.1 (OMe ester), 42.6 (C-12), 39.1 (C-15), 29.6 (C-3), 29.3, 29.2 (C-13, C-14), 22.6 (C-2, C-11), 9.7 (C-16).

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