J. Braz. Chem. Soc., Vol. 8, No. 5, 505-508, 1997.
Printed in Brazil.

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0103 – 5053 $6.00 + 0.00

Article

Xanthones and Other Constituents of *Vismia parviflora*

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Received: August 28, 1996

Vismia parviflora, planta da família Guttiferae, é uma espécie da tribo Vismeae encontrada na região de Ouro Preto MG. Dos extratos benzênico e etanólico dos galhos e etanólico dos frutos de um especimen desta planta, cromatografados em sílica gel, foram isolados sitosterol, ácido betulínico, lupeol, friedelina, β-friedelinol, ácido chiquímico, ácido 3,4-diidroxibenzóico, quercetina e as antraquinonas madagascina, ácido crisofânico, vismiaquinona-A e vismiaquinona-C, além das xantonas 1,7-diidroxixantona e 1,5-diidroxi-8-metoxixantona. Estas substâncias tiveram suas estruturas elucidadas com base nos seus dados espectrométricos de IV, UV, EM e RMN de ^{1}H e ^{13}C uni-(1D) e bidimensional-(2D).

The stems and fruits of *Vismia parviflora* have been shown to contain sitosterol, betulinic acid, lupeol, friedelin, β-friedelinol, shikimic acid, 3,4-dihydroxybenzoic acid, quercetin, 1,7-dihydroxyxanthone, 1,5-dihydroxy-8-methoxyxanthone, madagascine, chrysophanic acid, vismiaquinone-A and its isomer vismiaquinone-C. The structures of these compounds have been elucidated by using spectroscopic data as MS, UV, IR, one- and two-dimensional NMR.

Keywords: Vismia parviflora, *Guttiferae, xanthone, anthraquinone, quercetin, terpenoids*

Introduction

According to Engler[1], *Vismia parviflora* belongs to the Guttiferae family, subfamily Hyperiocoideae, tribe Vismieae. The *Vismia* genus consists of small trees inhabiting the tropical and subtropical regions of South and Central America, where they are used in folk medicine as strong purgative, whereas their barks are considered to be tonic and febrifugal[2-3].

Although the chemistry of the Guttiferae family has been widely studied[4], no more than fifteen species of *Vismia* have been investigated among the fifty known species. Several species of this genus have been shown to contain xanthones and anthranoides[5-10]. In the present study we have identified the chemical constituents from stems and fruits of *Vismia parviflora*, which have not been reported previously.

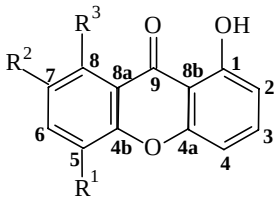
Results and Discussion

Fractionation of the ethanol extracts of stems and fruits on silica gel, followed by gel filtration and recrystalization, afforded the isolation the compounds **1**-**6**. The UV spectra of **1** and **2** exhibited absorption bands characteristic of xanthones[11]. The bathochromic shift observed upon addition of $AlCl_3$ indicated the presence of a chelated hydroxyl group at C-1 or C-8 for the both compounds **1** and **2**. The ^{1}H-NMR spectra of both **1** and **2** showed , absorptions at: δ 7.68 (t, J = 8.1 Hz H-3), 6.75 and 6.97(dd, J = 8.1 and 1,0 Hz H-2 and H-4) for **1** and δ 7.63(t, J = 7.30 Hz H-3), 6.72 and 6.94 (dd, J = 7.3 and 1.3 Hz H-2 and H-4) for **2**, indicative for both compounds the same three hydrogens vicinal pattern for one of the aromatic ring. In addition, the ^{1}H-NMR of compound **1** showed three *ortho*- and *meta*-coupled hydrogens at δ 7.50 (d, J = 8.8 Hz H-5), 7.40 (dd, J = 8.8 and 2.7 Hz H-6), 7.57 (d, J = 2.7 Hz H-8). The OH on C-7 was proposed by the absence of the bathochromic shift of the UV maxima in the presence of sodium acetate, and confirmed by methylation of **1** with an ether solution of diazomethane. The ^{13}C-NMR spectra was compatible with 1,7-dihydroxyxanthone **1**. The mass spectrum showed

Table 1. ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50 MHz) spectral data for the compounds 1-3 compared with literature 1a-3a.

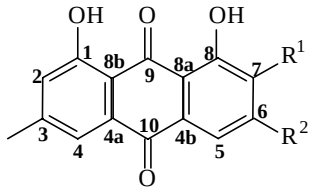
	Compound 1				Compound 2				Compound 3			
C	1 (acetone-d_6)		1a lit. [15]^{Q} ($CDCl_3$)		2 (acetone-d_6)		2a lit. [14]# ($CDCl_3$/CD_3OD 9:1)		3 ($CDCl_3$)		3a lit. [16]$^{!}$ ($CDCl_3$)	
	δ ^{13}C	δ ^{1}H	δ ^{13}C*	δ ^{1}H	δ ^{13}C	δ ^{1}H	δ ^{13}C*	δ ^{1}H	δ ^{13}C	δ ^{1}H	δ ^{13}C*	δ ^{1}H
1	163.0	---		---	161.9	---		---	162.4	---		---
2	110.4	6.75 dd(1.0; 8.1)§		6.77 dd(0.5; 8.4)	111.1	6.72 dd(1.3; 7.3)		6.76 dd(1.5; 8.0)	124.5	7.06 sl		7.08
3	138.0	7.68 t(8.1)		7.59 t(8.8)	136.1	7.63 t(7.3)		7.56 dd(1.5; 8.0)	136.9	---		---
4	107.0	6.97 dd(1.0; 8.1)		6.95 dd(0.5; 8.4)	106.1	6.94 dd(1.3; 7.3)		6.96 dd(1.5; 8.5)	124.4	7.61 sl		7.61
4a	157.0	---		---	153.1	---		---	133.1	---		---
4b	131.0	---		---	145.7	---		---	133.2	---		---
5	119.5	7.50 d(8.8)		7.41 d(9.3)	138.5	---		---	118.1	7.78 d(8.0)		7.80
6	126.0	7.40 dd(2.7; 8.8)		7.33 dd(2.9; 9.3)	121.1	7.32 d(7.3)		7.26 d(9.0)	121.3	7.64 t(8.0)		7.65
7	154.7	---		---	105.1	6.85 d(7.3)		6.66 d(9.0)	119.9	7.25 d(8.0)		7.27
8	108.0	7.57 d(2.7)		7.63 d(2.9)	154.8	---		---	162.6	---		---
8a	121.0	---		---	109.0	---		---	108.5	---		---
8b	109.0	---		---	110.7	---		---	107.3	---		---
9	181.5	---		---	182.5	---		---	191.8	---		---
10	---	---	---	---	---	---	---	---	181.7	---		---
OH	---	12.57; 9.20	---	12.62; 5.01	---	13.17; 8.70	---	12.97	---	12.10; 11.98		*
OMe	---	---	---	---	56.3	3.89 s		3.85 s	---	---		---
Me	---	---	---	---	---	---	---	---	22.2	2.44 s		*

§-Coupling constants (J in Hz) are given in parentheses. Θ - ^{1}H-NMR (200 MHz). # - ^{1}H-NMR (60 MHz). ! - ^{1}H-NMR (300 MHz). * - No value is provided.

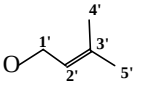


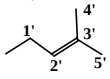
1 $R^1 = R^3 = H$; $R^2 = OH$

2 $R^1 = OH$; $R^2 = H$; $R^3 = OMe$



3 $R^1 = R^2 = H$

4 $R^1 = H$; $R^2 =$ 

5 $R^1 =$  ; $R^2 = OMe$

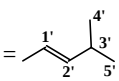
6 $R^1 =$  ; $R^2 = OMe$

Figure 1. Xanthones and anthraquinones isolated from Vismia parviflora.

Table 2. ^{1}H-NMR (200 MHz) and ^{13}C NMR (50 MHz) spectral data for the compounds 4-6 compared with literature 4a-6a.

	Compound 4				Compound 5				Compound 6			
C	4 ($CDCl_3$)		4a lit. [7]# ($CDCl_3$)		5 ($CDCl_3$)		5a lit. [10]! ($CDCl_3$)		6 ($CDCl_3$)		6a lit. [8]! ($CDCl_3$)	
	δ ^{13}C	δ ^{1}H	δ ^{13}C*	δ ^{1}H	δ ^{13}C	δ ^{1}H	δ ^{13}C*	δ ^{1}H	δ ^{13}C	δ ^{1}H	δ ^{13}C	δ ^{1}H
1	164.9	—		—	163.9	—		—	162.8	—	162.6	—
2	124.3	6.56 d(2.0)		6.50 d(2.0)	124.8	7.04 d(1.6)		7.02 s	124.3	6.93 sl	124.2	7.03 s
3	139.7	—		—	133.6	—		—	148.3	—	148.1	—
4	121.1	7.23 d(2.0)		7.13 d(2.0)	121.0	7.58 d(1.6)		7.55 s	121.0	7.24 sl	121.0	7.34 s
4a	133.1	—		—	133.6	—		—	131.9	—	133.0	—
4b	135.0	—		—	133.4	—		—	133.0	—	*	—
5	107.4	7.50 d(1.8)		7.43 d(2.0)	103.7	7.34 s		7.35 s	110.3	7.46 s	103.1	7.56 s
6	165.7	—		—	162.1	—		—	161.9	—	161.8	—
7	108.6	6.91 d(1.8)		6.95 d(2.0)	124.6	—		—	114.0	—	115.7	—
8	162.3	—		—	162.8	—		—	162.3	—	162.2	—
8a	108.0	—		—	111.1	—		—	110.4	—	110.3	—
8b	110.0	—		—	114.1	—		—	115.7	—	113.5	—
9	190.5	—		—	191.7	—		—	191.2	—	190.9	—
10	182.0	—		—	182.7	—		—	181.7	—	182.4	—
1’	65.6	4.54 d(6.4)§		4.58 d(7.0)	22,1	3.40 d(7.0)		3.40 d(7.0)	132.0	6.50 d(16.2)	131.8	6.60 d(16.0)
2’	118.1	5.40 dd(6.7)		5.40 t(7.0)	121.5	5.16 t(7.0)		5.18 t(7.0)	146.6	6.85 dd(7.0; 16.2)	146.5	6.95 dd(6.5; 16.0)
3’	143.5	—		—	126.3	—		—	33.4	2.40 m	33.4	2.48 m
4’	25.8	1.71 s		1.75 s	22.6	1.66 s		1.68 s	22.7	1.04 d(7.0)	22.5	1.14 d(6.5)
5’	18.3	1.75 s		1.75 s	22.5	1.78 s		1.80 s	22.4	1.05 d(7.0)	22.5	1.14 d(6.5)
OH	—	12.26; 12.10	—	12.03; 11.90	—	12.39; 12.12	—	12.40; 12.12	—	12.80; 11.96	—	12.84; 12.02
Me-3	22.1	2.34 s		2.38 s	20.5	2.42 s		2.44 s	22.1	2.34 s	22.1	2.42 s
OMe	—-	—	—	—	56.3	4.01 s		4.00 s	56.2	3.93 s	56.1	4.02 s

§ - Coupling constants (J in Hz) are given in parentheses. # - ^{1}H-NMR (60 MHz). ! - ^{1}H-NMR (100 MHz). * - No value is provided.

peak at m/z 228 ($[M]^{+\bullet}$), which is in accordance with the molecular formula $C_{13}H_8O_4$. For the compound **2** the ^{1}H-NMR showed two *ortho* coupled hydrogens at δ 6.85 and 7.32 (d, J = 7.3 Hz, H-7 and H-6 respectivelly), besides the singlet at δ 3.89 (3H, s, OCH_3). The ^{13}C-NMR was compatible with 1,5-dihydroxy-8-methoxyxanthone. The mass spectrum showed peak at m/z 258 ($[M]^{+\bullet}$, 96%) in accordance with molecular formula $C_{14}H_{10}O_5$, and the base peak at m/z 240 ($[M - 18]^{+\bullet}$, 100%). The loss of water from the $[M]^{+\bullet}$ is due to the operation of an *ortho* effect caused by the methoxy substituent at C-8[12], what is in agreement with the proposed structure. (Table 1).

Compounds **3**-**6**, appeared to be 1,8-dihydroxyanthraquinone derivatives based on their UV-Vis and the IR absorptions bands characteristic of anthraquinones[13]. The ^{1}H-NMR spectra of these compounds showed the same pattern of substitution for one of the aromatic ring, all of them showing two *meta*-coupling hydrogens, between δ 7.23 - 7.61 (H-4) and 6.59-7.06 (H-2), besides the methyl group at C-3 in δ 2.4 and a chelated hydroxy group at C-1 for all of them. The ^{1}H-NMR spectra of compounds **4** and **5** showed signals compatible with a γ,γ‘-dimethylallyl side chain, an O-dimethylallyl at C-6 for **4,** whereas **5** has a dimethylallyl at C-7. In addition compound **5** showed a methoxy group at 4.01 and an aromatic hydrogen at δ 7.34 (s, H-5). For compound **6** the ^{1}H-NMR spectra showed signals in accordance with the presence of a Δ^1- isopentenyl

side chain at C-7, a methoxy group at δ 3.93 and an aromatic hydrogen at δ 7.46 (s, H-5). (Table 2).

Experimental

Plant material, A specimen of *Vismia* was collected in Três Moinhos district, Ouro Preto city, State of Minas Gerais, Brazil, in March 1986. The specimen was identified by Prof. José Badini, botanic garden of the Universidade Federal de Ouro Preto - Brazil.

Extraction and isolation of the constituents from stems: Air-dried, powdered stems (1,400 g) were extracted with C_6H_6 followed by EtOH. Removal of the solvents gave 9.4 g and 22.0 g as residues respectively. The benzene extract was chromatographed on silica gel (200.0 g), elution was performed with C_6H_6 , EtOAc and EtOH. Several frs. were collected and sepd. into ten groups (A_1-A_{10}), by TLC. A_1 (0.36 g) was purified by rechromatography and recrystalization from acetone yielding friedelin (10.0 mg) and β-friedelinol (7.0 mg). A_7 (0.20 g) was rechromatographed on silica gel (10.0 g), using C_6H_6 , $CHCl_3$ and EtOAc as eluents, giving sitosterol (24.4 mg,), 1,7-dihydroxyxantone (**1**, 1.5 mg, mp 240-241° from EtOH, Lit.[14] 240-241° from $CHCl_3$) and betulinic acid (15.0 mg). The ethanol extract (22.00 g), was chromatographed on silica gel (450.0 g), with hexane, EtOAc and EtOH as eluents, giving chrysophanic acid (**3**, 8.5 mg, mp 191-193° from acetone), friedelin (12.0 mg), β-friedelinol (8.0 mg), madagascine (**4**, 12.0 mg, mp 149.5-152.0° from acetone, Lit.[7] mp 154-156°) 1,7-dihydroxyxantone (**1**, 12.0 mg) betulinic acid (15.0 mg) and 1,5-dihydroxy-8-methoxyxantone (**2**, 8.0 mg, mp 228,0-229,8° from EtOH, Lit [14] mp 230-231° from $CHCl_3$).

Extraction and isolation of the constituents from fruits: The fruits of *Vismia parviflora*, were dried and ground to a powder (56.80 g), which was throughly extracted with EtOH. Removal of solvent gave a residue (16.94 g), which was chromatographed on silica gel (370.00 g) using hexane, EtOAc and EtOH as eluents. Several frs. were collected and sepd. into five groups (B_1-B_5) by TLC. B_2 (0.56 g) was washed with Me_2CO and the insoluble portion (32.2 mg) recrystalized in EtOH giving vismiaquinone A (**6**, 18.0 mg, mp 197.3-198.7° from acetone, Lit[8] mp 202-204° from petrol/EtOAc 19:1). The remaining soluble portion (0.40 g), was purified by prep. TLC (layer thickness 1.0 mm), giving vismiaquinone C (**5**, 12.0 mg, mp 212,4-214,6° from acetone, Lit.[10] 215-217° from acetone), and madagascine (**4**, 13.5 mg). B_3 (0.21 g), was recrystalized in EtOH giving chrysophanic acid (**3**, 17.0 mg). B_4 (0.23 g) was rechromatographed on sephadex LH 20 (sigma) with MeOH as eluent, yielding quercetin (23.0 mg) and 3,4-dihydroxybenzoic acid (13.0 mg). B_5 (4.30 g) was washed exhaustively with EtOH, giving shikimic acid (0.52 g).

Acknowledgments

Financial support from the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), and Coordenação de Aperfeiçoamento Pessoal de Ensino Superior (CAPES) is gratefully acknowledged. The authors also thank anonymous referee for constructive suggestions.

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