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Note

The Complete Assignment of ^{1}H- and ^{13}C-NMR of Prenylated Xanthones from *Tovomita spp.* (Guttiferae)

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A 1,6-dihidroxy-5-(3-metilbut-2-enil)-6',6'-dimetil-pirano(2',3';7,8)- 6",6"- dimetil-pirano (2",3";3,2)xantona e a 1,3,6-trihidroxi-6',6'-dimetil-pirano(2',3';7,8)-2,5-di-(3-metilbut-2-enil)xantona tiveram seus deslocamentos químicos de hidrogênio e carbono-13 atribuídos de forma inequívoca, com base nas informações obtidas através dos espectros de RMN de ^{1}H[1D e 2D(^{1}H-^{1}H-COSY) e de correlação heteronuclear ^{1}H-^{13}C-COSY[$^{n}J_{CH}$(n = 1, 2 e 3)]. Estes dados ainda foram confirmados utilizando-se a técnica de NOE diferencial.

The ^{1}H-and ^{13}C-NMR spectral data of 1,6-dihydroxy-5-(3-methylbut-2-enyl)-6',6'-dimethyl-pyrano(2',3';7,8)-6",6"-dimethyl-pyrano(2",3";3,2)xanthone and 1,3,6-trihydroxy-6',6'-dimethyl-pirano(2',3';7,8)-2,5-di-(3-methylbut-2-enyl)xanthone have been unambiguously assigned by the analysis of homonuclear (^{1}H-^{1}H-COSY) and heteronuclear [^{1}H-^{13}C-COSY: modulated with $^{1}J_{CH}$ and $^{n}J_{CH}$ (n = 2 and 3, COLOC)] shift-correlated and NOE difference spectra.

Keywords: *Tovomita, Guttiferae, prenylated xanthone, NMR data*

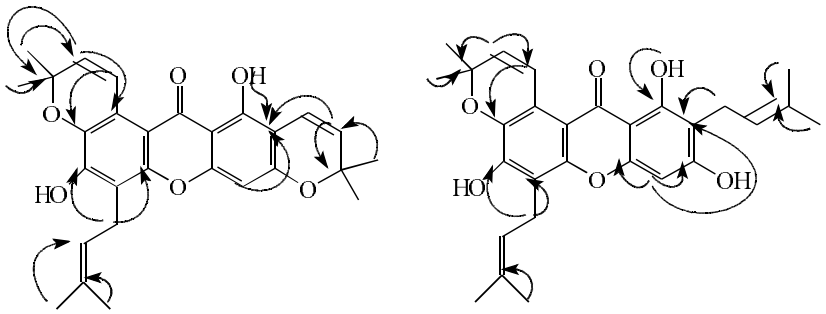
Introduction

Several compounds have been isolated from two species of *Tovomita* (*T. macrophylla* and *T. pyrifolium*)[1,2]. Among them, two prenylated xanthones, the structures of which were defined as 1,6-dihydroxy-5-(3-methylbut-2-enyl)-6',6'-dimethyl-pyrano(2',3';7,8)-6",6"-dimethyl-pyrano (2",3" ;3,2)xanthone (**1**) and 1,3,6-trihydroxy-6', 6'-dimethyl-pyrano(2',3';7,8)-2,5-di-(3-methylbut-2-enyl)xanthone (**2**). Despite the fact that xanthones have been studied by ^{1}H-and ^{13}C-NMR spectroscopy, these structures have not been previously studied using these methods. This investigation led us to confirm the proposed structures and unambiguously establish the chemical shifts for the protons and carbons.

Experimental

1D and 2D NMR spectra were recorded at 200 MHz for ^{1}H, and at 50.3 MHz for ^{13}C, using a Bruker AC-200 spectrometer. The pulse sequences used are contained in the XHCORR > AU Bruker program for heteronuclear correlation (^{1}H-^{13}C-COSY), with $D_3 = 0.5/J_{CH}$ and $D_4 = 0.25/J_{CH}$, modulated for $^{1}J_{CH} = 135$ Hz and $^{n}J_{CH} = 8.0$ Hz (long range, n = 2 and 3). The COSY.AU program was ap-

(*) The authors dedicate this article to the memory of Professor Mesquita, for his contributions to the field of xanthones.



(**1**) (**2**)

Figure 1. Long-range heteronuclear correlations observed for 1 and 2.

Table 1. ^{1}H- (200 MHz) and ^{13}C (50.3 MHz) NMR spectral data of compound 1 (DMSO-d_6, 40 °C, δ ppm, J = Hz).

Position	δ_C[a]	δ_H (J,Hz) and ^{1}H -^{13}C-COSY($^{1}J_{CH}$)	^{1}H-^{1}H-COSY	NOE (%)
1	159.4 (C)			
2	103.7 (C)			
3	157.2 (C)			
4	93.8 (CH)	6.13 (s)		
4a	156.0 (C)			
10a	150.6 (C)			
5	115.1 (C)			
6	150.3 (C)			
7	137.6 (C)			
8	116.9 (C)			
9	182.2 (C)			
8a	107.0 (C)			
9a	103.2 (C)			
4’	120.5 (CH)	7.80 (d, 10.0)	H-5’	
5’	131.8 (CH)	5.70 (d, 10.0)	H-4’	
6’	75.7 (C)			
7’	26.1 (CH_3)	1.38(s)		H-5’(4.0)
8’	26.1 (CH_3)	1.38(s)		H-5’(4.0)
4”	115.1 (CH)	6.50 (d, 10.0)	H-5’’	
5”	127.4 (CH)	5.55 (d, 10.0)	H-4’’	
6”	77.8 (C)			
7”	28.1 (CH_3)	1.36 (s)		H-5’’(1.0)
8”	28.1 (CH_3)	1.36 (s)		H-5’’(1.0)
1”’	22.3 (CH_2)	3.40(d)	H-2”’	H-2’’’(10.0); H-4’’’(6.0)
2”’	121.4 (CH)	5.13(t)	H-1”’	H-5’’’(7.0)
3”’	131.5 (C)			
4”’	17.8 (CH_3)	1.76(s)		H-5’’’(3.0); H-1’’’(3.0)
5”’	25.5 (CH_3)	1.57(s)		H-2’’’(7.0); H-4’’’(4.0)
1-OH	-	13.26(s)		

[a]The hydrogenation patterns was deduced by DEPT (Θ = 90 ° and 135°).

Table 2. ^{1}H- (200 MHz) and ^{13}C (50.3 MHz) NMR spectral data of compound 2 (DMSO-d_6, 40 °C, δ ppm, J = Hz)

Position	δ_C[a]	δ_H (J,Hz) and ^{1}H -^{13}C-COSY($^{1}J_{CH}$)	^{1}H-^{1}H-COSY	NOE (%)
1	159.6 (C)			
2	109.6 (C)			
3	162.4 (C)			
4	92.3 (CH)	6.35 (s)		
4a	154.3 (C)			
10a	150.2 (C)			
5	115.4 (C)			
6	149.9 (C)			
7	137.3 (C)			
8	116.9 (C)			
9	181.8 (C)			
8a	106.7 (C)			
9a	101.9 (C)			
4’	120.4 (CH)	7.84 (d, 10.0)	H-5’	H-5’(11.0)
5’	131.9 (CH)	5.85 (d, 10.0)	H-4’	H-4’(19.0); H-7’,8’(10.0)
6’	75.4 (C)			
7’	26.6 (CH_3)	1.40(s)		
8’	26.6 (CH_3)	1.40(s)		
1”	21.0 (CH_2)	3.18(d)	H-2”	H-4’’(7.9)
2”	122.6 (CH)	5.16 multipl. covered	H-1”	H-5’’(12.0)
3”	130.3 (C)			
4”	17.7 (CH_3)	1.60 (s)	H-2’’	
5”	25.5 (CH_3)	1.69 (s)		
1”’	22.2 (CH_2)	3.42(d)	H-2”’, H-4’’’	
2”’	121.4 (CH)	5.16(t)	H-1”’, H-4”’	H-5’’’(12.0)
3”’	131.3 (C)			
4”’	17.7 (CH_3)	1.82(s)	H-1”’, H-2”’	
5”’	25.5 (CH_3)	1.61(s)		
1-OH	-	13.58(s)		

[a]The hydrogentaion patterns was deduced by DEPT (Θ = 90° and 135°).

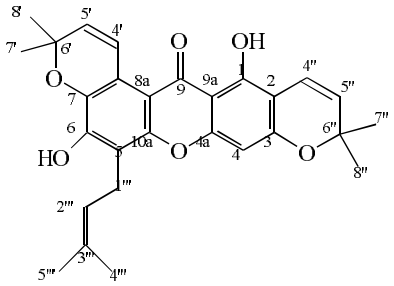
plied for homonuclear (^{1}H-^{1}H-COSY), NOEDIFF.AU to observe NOE, and signal multiplicities were established by DEPTVAR.AU (Θ = 90° and 135°).

Results and Discussion

The observed signals in the NMR ^{1}H-spectra [1D and 2D (^{1}H-^{1}H-COSY)], in conjunction with the observed interaction in the heteronuclear correlation spectra ^{1}H-^{13}C-COSY[$^{n}J_{CH}$ (n = 1,2 and 3)] (Tables 1 and 2, Fig. 1), were compatible with the presence of two pyrano and one prenyl unit in Structure **1**, and one pyrano and two prenyl units in Structure **2**.

The carbon chemical shift data for the xanthone skeleton obtained by ^{13}C-NMR (PND) from **1** and **2** (Tables 1 and 2) when compared to models **3**[3] and **4**[4], showed the same substitution pattern on ring A of **1** and **2** respectively. The location of the pyrano units in **1** and the prenyl units in **2** was confirmed by long-range heteronuclear chemical shift correlation (Fig. 1). The long-range coupling between H-1” (δ 3.18), 1-OH(δ 13.58), H-4(δ 6.15), and C-2(δ 109.6) in Structure **2** are in accordance with ring A non-substituted at C-4 position. Consequently, the long-range coupling between H-5”(δ 5.55) and C-2(δ 103.7) in structure **1** (Fig. 1) confirms the same hydrogenation pattern of ring A.

The other ^{13}C signals of the xanthone skeleton were non-hydrogenated. Two of them are oxygenated carbons (δ 150.3 and 137.6) of **1** and (δ 149.9 and 137.3) of **2**, and two



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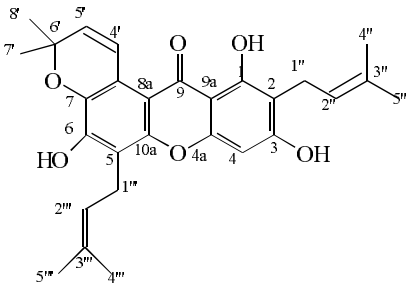

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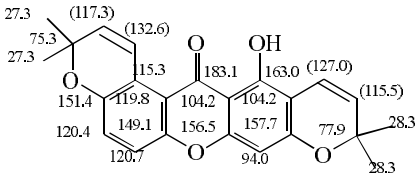

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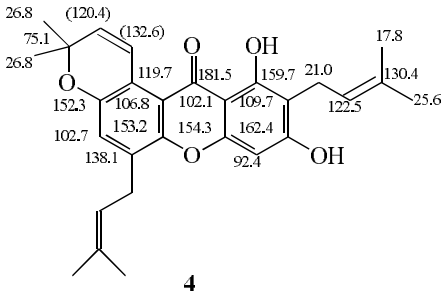

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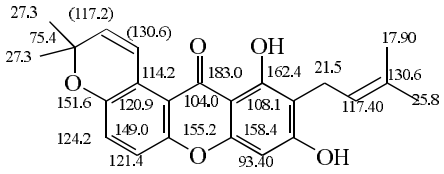

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did not have any heteroatom attached to them (δ 115.1 and 116.9) for **1** and (δ 115.4 and 116.9) for **2**, which are in accordance with a fully substituted ring B.

The long-range coupling between H-1''' (δ 3.40) and C-10a (δ 150.6), and H-1''' (δ 3.40) and C-6 (δ 150.3) of **1**, and H-1''' (δ 3.42) and C-6 (δ 149.9) of **2** are in accordance with the prenyl unit attached to C-5. The same kind of observation was made in relation to H-4' (δ 7.80) and C-7 (δ 137.6) of **1** and H-4' (δ 7.84) and C-7 (δ 137.3) of **2** which was in accordance with the presence of the pyrano unit at C-7/C-8. In addition the hydroxyl group should be attached at C-6. This experimental information suggests that the attribution of the chemical shift for C-4' and C-5' reported in the literature for **3**[3,5] an **5**[5] must be exchanged.

The observed NOE for **1**, with double irradiation, defined the attribution of methyl groups from pyrano and prenyl units of **1** and **2** (Tables 1 and 2). In the prenyl units, NOE experiments were very important for establishing the stereochemistry of the methyl groups. In Structure **1**, the irradiation in the H-1''' frequency generated NOE of 10.0 and 6.0 % in H-2''' and H-4''', respectively. On the other hand, irradiation in the frequency of H-2''' gives a NOE of 7.0% in H-5''', while the irradiation of the H-4''' signal gives a NOE of 3.0 % in H-1''' and H-5'''. Again, irradiation at the frequency of H-5''' produces NOE of 7.0 and 4.0 % in H-2''' and H-4''', respectively (Table 1).

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