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C-prenylflavonoids from roots of *Tephrosia tunicata*

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Abstract

A 3′,3′-di-(γ,γ-dimethylallyl)-2′, 4′-di-oxo-enolchalcone (tunicatachalcone) and five known C-prenylflavonoids were isolated and/or identified from the roots of *Tephrosia tunicata*. Their structures were established by spectral methods and chemical transformation.

Keywords: *Tephrosia tunicata*; Leguminosae; Roots; Chalcones; Flavanones; Flavone; Rotenoids; Spectral data

1. Introduction

Our phytochemical investigation of plants of the genus *Tephrosia* was initiated with *Tephrosia candida*, where rotenoids were mainly isolated (Andrei et al., 1997). Using the standard methods to isolate flavonoids from *T. candida*, analytical methodology was developed for identification and quantification of insecticidal rotenoids (Fukami and Nakagima, 1971) using GC–MS without derivatization (Pereira et al., 1998).

In continuing the study of *Tephrosia* species with the aim to find potential sources of insecticidal plants, we describe isolation of a new 3′,3′-di-(γ,γ-dimethylallyl)-2′,4′-di-oxo-chalcone **1** and the six previously know C-prenylated flavonoids **2**–**6**, including a pair of tautomeric chalcones, from roots of *T. tunicata*. Their structures were deduced from spectral data, including 2D NMR ^{1}H–^{1}H COSY and ^{13}C–^{1}H COSY experiments. The nomenclature and numbering of the compounds follows that of Harborne (1988); i.e. "7, 8 and 9" rather than "α, β and C=O", respectively (Dagne et al, 1988).

2. Results and discussion

A new enolchalcone, which was named tunicatachalcone **1**, and five known compounds **2**–**6** were isolated from an *n*-hexane extract of the roots of *T. tunicata* by a combination of chromatographic techniques. The known compounds were identified by comparison of physical and spectral data (m.p., EIMS, IR, ^{1}H and ^{13}C NMR spectral values) with those reported in the literature. In this regard, candidin **6** was first reported by Chibber and Dutt (1981), but was later named isopongaflavone by Garcez et al. (1988). The trivial names, obovatachalcone, obovatin, and obovatin methyl ether, were assigned to compounds **3**, **4**, and **5**, respectively, by Chen et al. (1978), although compound **5**, was later named pongachin by Chibber and Dutt (1981). The reports of pongochalcone-I from *T. candida* (Chibber et al., 1981), *Dahhlstedtia prinnata*, and *D. pentaphylla* (Garcez et al., 1988) give rise to additional confusion: the spectral and chemical data agree better with those of obovatachalcone **3** than with those of pongachalcone-I, which was first reported from *Pongamia glabra* by Subrahmanyam et al. (1973).

Tunicatachalcone **1**, was characterized by ^{1}H, ^{13}C [HBBD and DEPT], ^{1}H–^{1}H COSY, and ^{13}C–^{1}H COSY and long range COLOC (Fig. 1). The ^{1}H and ^{13}C NMR spectra resembled to those reported for chalcones **2** and **3** (Table 1). The major distinction between these natural products was in the different chemical shifts attributed to the hydroxyl groups at: C-9 of **1** (δ_H 15.15) and C-2′ of **2** (δ_H 13.67), the presence of two carbonyl groups [δ_C 205.56 (*s*) and 198.09 (*s*)] and two γ,γ-dimethylallyl moieties in **1** [δ_C 38.19 (*t*, CH_2-1″, CH_2-1‴), 118.00 (*d*, CH-2″, CH-2‴), 134.85 (*s*, C-3″, C-3‴), 17.82 (*q*, CH_3-4″, CH_3-4‴) and 25.79 (*q*, CH_3-5″, CH_3-5‴); δ_H 2.66 (*d*,

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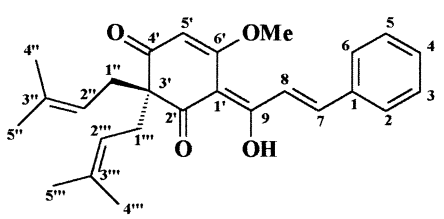

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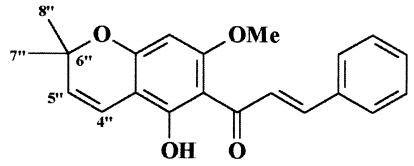

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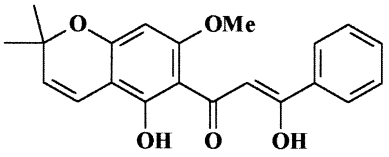

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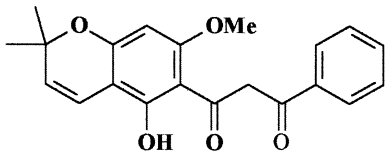
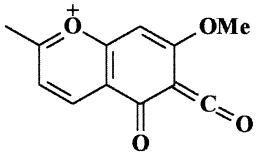


2a



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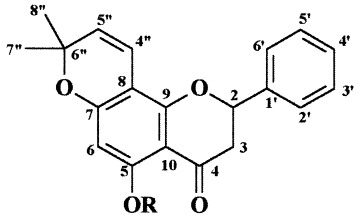
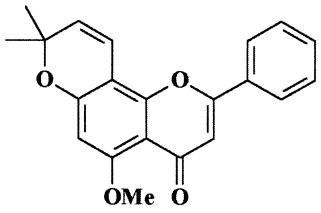


4 R = H
4a R = Ac
5 R = Me



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$J = 7.4$ Hz, 2H-1″ and 2H-1‴), 4.86 (*t*, $J = 7.4$ Hz, H-2″ and H-2‴, 1.57 [*br s*, 3H (4″, 4‴, 5″ and 5‴)] linked to sp^3 C-3′ [δ_C 62.00 (*s*)]. The location of the two carbonyl groups at C-2′ and C-4′ was defined by ^{13}C–^{1}H COSY spectroscopy, which clearly showed spin–spin coupling ($^3J_{CH}$) between CH_2-1″/CH_2-1‴ (δ_H 2.66) and both C-2′ (δ_C 205.56) and C-4′ (δ_C 198.09). On the other hand, this argument, based on COLOC spectra, establishes the location of the enolic hydroxyl at C-9 in tunicatachalcone, contrary to literature reports, such as ceroptin (Star et al., 1975; Wollenweber and Dietz, 1980).

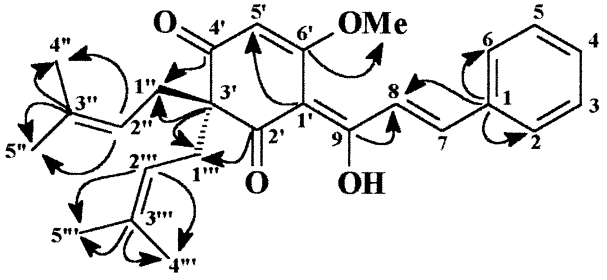

Fig. 1. Correlations observed with heteronuclear long-range coupling ^{13}C–^{1}H-COSY spectra (COLOC) of tunicatachalcone **1**. $^{13}C \rightarrow {}^{1}H$.

The other heteronuclear long-range couplings observed in this spectrum (shown in Fig. 1) involved the H-8 (δ_H 7.76) with C-9 (δ_C 178.94, $^2J_{CH}$, a chemical shift incompatible with a carbonyl group at C-9, e.g. as in chalcones **2** and **3**, H-1″/H-1‴ (δ_H 2.66) with C-3′ (δ_C 62.00, $^2J_{CH}$), 3H-4″/3H-4‴/3H-5″/3H-5‴ (δ_H 1.57) with C-3″/C-3‴ (δ_C 134.85, $^2J_{CH}$) and CH-2″/CH-2‴ (δ_C 118.00, $^3J_{CH}$), H-5′ (δ_H 5.53) with C-1′ (δ_C 105.50, $^3J_{CH}$) and MeO-6′ (δ_H 3.92) with C-6′ (δ_C 171.00, $^3J_{CH}$).

These data in combination: with the coupling constant ($J = 16.7$ Hz), used to establish the stereochemistry as *E* for the olefinic double bond; the ^{1}H–^{1}H COSY and ^{13}C–^{1}H COSY spectra (Table 1): and the NOE difference spectra by irradiating the resonance at δ_H 3.92, resulted in an enhanced signal of H-5′ (δ_H 5.53, NOE = 8.0%) unambiguously permitted deduction of structure **1** for the new chalcone derivative, tunicatachalcone.

The EIMS of this compound gave a molecular ion at *m/z* 406 ($[M]^+$ 26%, $C_{26}H_{30}O_4$) with other significant peaks at *m/z* 337, 295, 233 and 131 (Fig. 2). Interconversion of tunicatachalcone **1** into tautomers with a carbonyl group at C-9 or into cyclic may take place under *EI* condition. Fig. 2 shows the proposed fragmentation mechanism to explain the formation of the main peaks observed in the mass spectrum of this natural product.

Table 1
^{1}H (200 MHz) and ^{13}C (50.3 MHz) NMR spectroscopic data for chalcones **1**–**3**. Chemical shifts in δ (ppm), in $CDCl_3$ and TMS as internal standard[a]

	1			**2**		**2a**		**3**	
C/H	δ_C	δ_H	C/H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	134.85	–	1	134.50	–	136.61	–	135.46	–
2,6	128.37	7.58–7.60 (*m*)	2,6	128.06	7.88 (*dd*, 7.5, 1.4)	126.56	7.95 (*dd*, 8.4, 1.6)	122.21	7.56–7.82 (*m*)
3,5	128.98	7.40–7.42 (*m*)	3,5	128.70	7.39–7.57 (*m*)	128.70	7.39–7.57 (*m*)	128.76	7.36–7.42 (*m*)
4	130.46	7.40–7.42 (*m*)	4	131.64	7.39–7.57 (*m*)	133.28	7.39–7.57 (*m*)	129.91	7.36–7.42 (*m*)
7	143.22	7.85 (*d*, 16.7)	7	175.20		198.53		142.04	7.70 (*d* 15.6)
8	122.94	7.76 (*d*, 16.7)	8	98.17	7.31 (*s*)	54.69	4.53 (*s*)	127.54	7.80 (*d* 15.6)
9	178.94	–	9	193.74	–	194.30	–	192.52	–
1′	105.50	–	1′	103.00	–	104.40	–	105.92	–
2′	205.56	–	2′	159.57	–	159.57	–	160.26	–
3′	62.00	–	3′	104.40	–	105.30	–	102.82	–
4′	198.09	–	4′	161.96	–	161.96	–	162.49	–
5′	98.86	5.53 (*s*)	5′	91.77	5.93 (*s*)	91.77	5.80 (*s*)	91.43	5.86 (*s*)
6′	171.00	–	6′	161.64	–	161.14	–	162.49	–
1″,1‴	38.19	2.66 (*d*, 7.4)	4″	115.79	6.68 (*d*, 10.0)	116.12	6.65 (*d*, 10.0)	115.94	6.62 (*d*, 10.0)
2″,2‴	118.00	4.86 (*d*, 7.4)	5″	125.45	5.45 (*d*, 10.0)	125.45	5.45 (*d*, 10.0)	125.24	5.40 (*d*, 10.0)
3″,3‴	134.85	–	6″	78.30	–	78.30	–	78.12	–
4″,4‴	17.82	1.57 (*br s*, 3)	7″	28.32	1.45 (*s*)	28.32	1.43 (*s*)	28.30	1.439 (*s*)
5″,5‴	25.79	1.57 (*br s*, 3)	8″	28.32	1.45 (*s*)	28.32	1.43 (*s*)	28.30	1.39 (*s*)
MeO-6′	56.08	3.92 (*s*)	MeO-6′	55.87	3.91 (*s*)	55.41	3.42 (*s*)	55.74	3.86 (*s*)
HO-2′	–	–	HO-2′	–	13.67 (*s*)	–	13.97 (*s*)	–	14.45 (*s*)
HO-9	–	15.15 (*s*)	HO-7	–	15.48 (*s*)				

[a] Multiplicity of signals of carbon atoms was deduced by comparative analysis of HBBD- and DEPT-^{13}C NMR spectra. Homonuclear 2D ^{1}H–^{1}H–COSY was also used for these assignments. Chemical shifts and coupling constants (*J*, in parentheses) of hydrogen atoms obtained from 1D ^{1}H NMR.

Table 2
^{1}H (200 MHz) and ^{13}C (50.3 MHz) NMR spectroscopic data for flavonoids **4**, **4a**, **5** and **6**. Chemical shifts in δ (ppm), in $CDCl_3$ and TMS as internal standard[a]

	4		**4a**		**5**		**6**	
C/H	δ_C	δ_H (*J*, Hz)	δ_C	δ_H (*J*, Hz)	δ_C	δ_H	δ_C	δ_H (*J*, Hz)
2	78.97	5.45 (*dd*, 12.5, 3.3)	78.97	–	78.84	5.39 (*dd*, 12.6, 3.4)	159.74	–
3	43.19	3.10 (*dd*, 16.7, 12.5, H_{ax}) 2.81 (*dd*, 16.7, 3.3, H_{eq})	43.19	6.67	45.52	2.95 (*dd*, 16.5, 12.5 H_{ax}) 2.75 (*dd*, 16.5, 3.4 H_{eq})	107.93	6.67 (*s*)
4	196.00	–	196.00	–	189.10	–	176.60	-
5	157.00	–	157.00	–	162.05	–	157.12	–
6	97.55	5.99 (*s*)	97.55	6.34	93.70	6.02 (*s*)	95.90	6.34 (*s*)
7	164.00	–	164.00	–	159.93	–	159.10	–
8	102.00	–	102.00	–	102.80	–	101.95	–
9	162.00	–	162.00	–	158.71	–	153.01	–
10	103.00	–	103.00	–	105.59	–	101.95	–
1′	139.00	–	139.00	–	138.88	–	130.67	–
2′,6′	125.91	7.40–7.44 (*m*)	125.91	7.81–7.91 (*m*)	125.85	7.28–7.43 (*m*)	124.93	7.81–7.91 (*m*)
3′,5′	128.72	7.40–7.44 (*m*)	128.72	7.51–7.64 (*m*)	128.63	7.28–7.43 (*m*)	128.18	7.51–7.64 (*m*)
4′	128.66	7.40–7.44 (*m*)	128.66	7.51–7.64 (*m*)	128.42	7.28–7.43 (*m*)	130.39	7.51–7.64 (*m*)
4″	115.48	6.53 (*d*, 10.1)	115.48	6.86 (*d*, 10.1)	115.93	6.56 (*d*, 10.1)	114.53	6.86 (*d*, 10.1)
5″	126.39	5.40 (*d*, 10.1)	126.39	5.63 (*d*, 10.1)	126.24	5.42 (*d*, 10.1)	126.79	5.63(*1*, 10.1)
6″	78.08	–	78.08	–	77.90	–	77.27	–
7″	28.18	1.41 (*s*)	28.18	1.50 (*s*)	28.11	1.40 (*s*)	27.47	1.50 (*s*)
8″	28.42	1.43 (*s*)	28.42	1.50 (*s*)	28.42	1.42 (*s*)	27.47	1.50 (*s*)
HO-5	–	12.11 (*s*)	–	–	–	–	–	–
AcO-5	–	–	–	–	–	–	–	–
MeO-5	–	–	–	3.95 (*s*)	56.07	3.85 (*s*)	55.88	3.95 (*s*)

[a] Multiplicity of signals of carbon atoms was deduced by comparative analysis of HBBD- and DEPT-^{13}C NMR spectra. Homonuclear 2D ^{1}H–^{1}H–COSY was also used for these assignments. Chemical shifts and coupling constants (*J*, in parentheses) of hydrogen atoms obtained from 1D ^{1}H NMR.

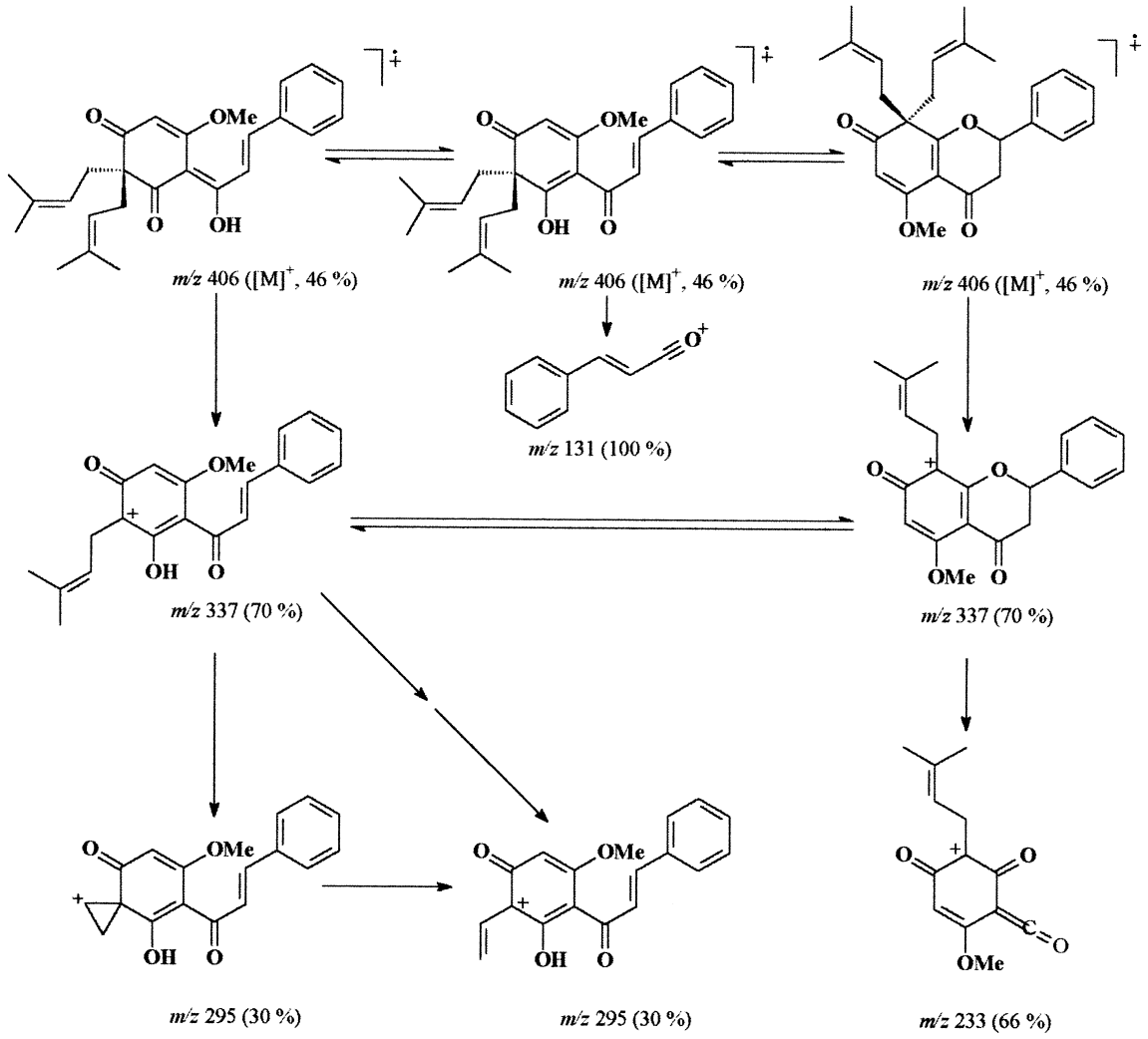

Fig. 2. Proposed fragmentation pathways for tunicatachalcone **1** (only peaks classified as major) by EIMS.

Thus, for example, the presence of a *m/z* 233 with a high intensity is easily explained by a "Retro-Diels-Alder" reaction type of a flavanonoid precursor.

The existence of the tautomeric chalcones **2** and **2a** was inferred from spectral data (Table 1), These compounds were previously isolated from *Lonchocarpus costaricences* (Waterman and Mahmoud, 1985) and also obtained by chemical transformation (Camele et al., 1980). GC–EIMS analysis revealed molecular ions with *m/z* 352 (14%, $C_{21}H_{20}O_5$) for both tautomers. Other prominent peaks were observed at *m/z* 337 (42%, M–Me) and at *m/z* 217 (100%), with the latter being consistent for fragment **2b**.

With respect to compound **3**, the ^{13}C–^{1}H COSY results clearly showed connectivity of C-7 (δ_C 142.04) to H-7 (δ_H 7.70) and C-8 (δ_C 127.54) to H-8 (δ_H 7.80). This observation led us to assume that the H-8 proton of compound **3** experiences anisotropic effects from two aromatic rings. These effects, together with the electron-withdrawing effect of the carbonyl group, cause deshielding of H-8, resulting in a shift downfield of the H-7 signal (Dantas et al., 1984). Our results suggest that the H-7/H-8 doublets were incorrectly assigned (i.e. $\delta_{H\text{-}7}$ 7.80 and $\delta_{H\text{-}8}$ 7.70) in a previous NMR spectroscopic analysis of obovatachalcone **3** (Chen et al., 1978).

The NMR spectral data of flavanones **4** and **5**, were in agreement with reporter data for these compounds (Chen et al., 1978). The assignments of the ^{1}H and ^{13}C resonances of compound **4**, was facilitated by comparison of the NMR spectroscopic data of its acetate derivative, **4a** (Table 2).

Some authors have discussed the difficulties in determining the position of dimethylchromene rings, whether angular or linear position, when there are O-substitutions at C-5 (Shirataky et al., 1985; Lin and Kuo, 1993). The angular position of the dimethylchromene ring in compound **5** followed from an NOE enhancement of H-6 (δ_H 6.02, 11%) upon irradiation of the 5-OMe signal at δ_H 3.85. The position of the dimethylchromene ring in compound **4** was determined by comparison with literature data and by ^{1}H–^{13}C HMBC spectroscopic analysis. In a recent review, Nomura and Fukai (1998) stated

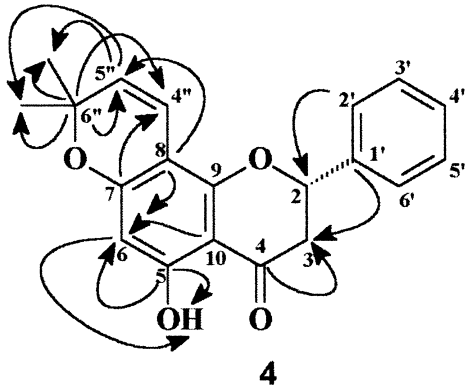

Fig. 3. Correlations observed with heteronuclear long-range coupling ^{13}C–^{1}H-COSY spectra (HMBC) of obovatin **4**, (Andrei, 1997).

that the value of the chemical shift of the OH-5 signal is ca. 12.09 in angular dimethylchromenoflavones. This value is in agreement with our results (Table 2). A correlation between the phenolic hydroxyl OH-5 and C-6 (Fig. 3) in the HMBC spectrum of **4** was taken as further evidence for the angular structure. The use of HMBC spectroscopy to solve such positional problems has been described previously (Andrei et al., 1997).

3. Experimental

M.p.s: uncorr. were obtained on a Kofler apparatus type; ^{1}H (200 MHz), ^{13}C NMR (50.3 MHz) spectra were recorded on a Bruker AC-200 spectrometer and HMBC on a Bruker ARX-400 ^{1}H (400 MHz), ^{13}C (100 MHz) spectrometer, using $CDCl_3$ as solvent and TMS as int. standard; EIMS: direct inlet with 70 eV ionization; CC: silica gel (Merck 0.05–0.70 mm); TLC: silica gel H or G (Merck); spots were visualized by UV (254 nm), by exposure to iodine vapour and after spraying with Ce_2SO_4/H_2SO_4.

3.1. Plant material

The roots of a specimen of *T. tunicata* were collected, in March 1989, at the Instituto Agronômico do Paraná de Londrina, Paraná, Brazil, and identified by Sueli de Carvalho, M.Sc. (IAPAR, Londrina, Paraná, Brazil).

3.2. Isolation of constituents

Exhaustive extraction of the powdered roots (3.1 kg) with *n*-hexane (at room temp. and the solvent removed in vacuo) yielded 17.7 g of crude extract. This *n*-hexane extract was applied to a silica gel (354 g) column, using *n*-hexane, *n*-hexane–CH_2Cl_2, CH_2Cl_2 and CH_2Cl_2–MeOH, as eluents, resulting in 16 groups of combined fractions. Chromatography of the fractions using the same or similar (changing sometimes CH_2Cl_2 for EtOAc) systems of elution, followed by TLC as a final purification step, furnished the following amounts of compounds: **1** (32 mg); **2** + **2a** (61 mg); **3** (127 mg); **4** (79 mg); **5** (250 mg) and **6** (168 mg).

3.3. 3′,3′-Di-(γ,γ-dimethylallyl)-2′,4′-di-oxo-enolchalcone, (tunicatachalcone) 1

M.p. 68–69°C; IR ν_{max} (KBr) cm^{-1}: 3480 (OH), 1645 and 1620 (CO at C-4′ and C-2′); ^{1}H and ^{13}C NMR: see Table 1; EIMS *m/z* (rel. int.): 406 ($[M]^+$, 25), 337 (70), 295 (30), 233 (66), 131 (100), 103 (57), 69 (46): see Fig. 2.

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