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6-[ω-arylalkenyl]-5,6-dihydro-α-pyrones from *Cryptocarya moschata* (Lauraceae)

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Abstract

Eleven 6-[ω-arylalkenyl]-5,6-dihydro-α-pyrones, cryptomoscatones D2, E1, E2, E3 and F1 and cryptopyranmoscatones A1, A2, A3, B1, B2 and B4, in addition to goniothalamin and cryptofolione, were isolated from branch and stem bark of *Cryptocarya moschata*, Lauraceae. Their structures were established by spectroscopic methods. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: *Cryptocarya moschata*; Lauraceae; 6-[ω-arylalkenyl]-5,6-dihydro-α-pyrone; Cryptomoscatone; Cryptopyranmoscatone; Cryptofolione; Goniothalamin; Styryl-pyrone

1. Introduction

Cryptocarya moschata (Lauraceae) is a tree growing up to 30–40 m high, which is found in the Atlantic Forest, mainly in the Southeastern Region of Brazil. It is popularly known as ''canela batalha'', ''canela branca'', ''canela noz-moscada'', ''nhutinga-branca'' or ''anhuvinha-branca''.

Cryptocarya spp. contain alkaloids, and some species have α-pyrones as additional secondary metabolites. Indeed, the occurrence of 5,6-dihydro-α-pyrones (substituted at C6 by alkyl or arylalkyl groups) has been noted in 13 botanical families and 20 species of fungi (Davies-Coleman & Rivett, 1989). These metabolites are biosynthesized from either acetate or mixed acetate–shikimate pathways (Leete, Muir & Towers, 1982).

Naturally occurring 6-aryl-5,6-dihydro-α-pyrones originating from the mixed biosynthetic pathway have been observed in only six genera: *Aniba* (Franca, Gottlieb & Suarez, 1973) and *Cryptocarya* (Lauraceae), *Goniothalamus* (Annonaceae), *Piper* (Piperaceae), *Psilotum* and *Tmesipteris* (Psilotaceae) (Davies-Coleman & Rivett, 1989).

The 6-aryl- or 6-arylalkyl-5,6-dihydro-α-pyrones from lauraceous species are characteristics of *Aniba* and *Cryptocarya* species. The α-pyrones of *Aniba* sp. possess a C4 methoxyl group, and a saturated or unsaturated carbonaceous side chain on C6. On the other hand, the pyrones of *Cryptocarya* are not substituted on C4 and instead have a styryl group attached to the C6 side chain. Some 5,6-dihydro-α-pyrones derived only from the acetate pathway, were also found in *Cryptocarya* species (Drewes, Horn & Mavi, 1997; Drewes, Horn & Wijewardene, 1996; Drewes, Horn & Scott-Shaw, 1995).

The present work describes the occurrence of 13 6-[ω-arylalkenyl]-5,6-dihydro-α-pyrones, including the known goniothalamin (**1**) and cryptofolione (**2**), and 11 new pyrones (**3**–**13**) in the branch and stem bark of *C. moschata*.

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Table 1
^{1}H-NMR data of compounds **1**–**7** and **5a**, in $CDCl_3$, 200 MHz[a]

H	1	H	2	3	H	6	H	4	5	5a	H	7
3	6.09 *dt* (10, 2)	3	6.02 *dt* (10, 2)	6.03 *ddd* (10, 2, 1)	3	6.00 *br* d (9)	3	6.04 *dt* (10, 2)	6.02 *dt* (10, 2)	6.05 *dt* (10, 2)	3	6.00 *dt* (10, 1)
4	6.93 *dt* (10, 4)	4	6.89 *ddd* (10, 5, 4)	6.90 *ddd* (10, 5, 4)	4	6.90 *br dd* (9, 5)	4	6.88 *ddd* (10, 5, 4)	6.86 *ddd* (10, 5, 4)	6.88 *ddd* (10, 5, 4)	4	6.80 *dt* (10, 4)
5	2.54 *m*	5	2.37 *m*	2.39 *m*	5	2.30 *m*	5	2.46 *m*	2.42 *m*	2.45 *m*	5	2.40 *m*
6	5.10 *qd* (7, 1)	6	4.78 *dddd* (11, 9, 5, 3)	4.66 *dddd* (11, 9, 5, 3)	6	4.70 *m*	6	4.91 *bd q* (6)	4.88 *br q* (7)	4.90 *br q* (7)	6	4.90 *br q* (6)
							1′	5.69 *ddt* (16, 6, 1)	5.67 *ddt* (16, 7, 1)	5.72 *dd* (8, 6)	1′	5.70 *dd* (16, 6)
							2′	5.90 *dtd* (16, 7, 1)	5.87 *dtd* (16, 7, 1)	5.80 *m*	2′	5.90 *dt* (16, 7)
		1′	1.87 *m*	1.86 *m*	1′	1.70 *m*	3′	2.30 *t* (7)	2.29 *t* (7)	2.40 *m*	3′	2.30 *t* (7)
		2′	4.31 *m*	4.38 *m*	2′	4.30 *m*	4′	4.01 *qui* (7)	4.04 *qui* (7)	5.06 *m*	4′	4.00 *m*
		3′	1.75 *m*	1.67 *t* (6)	3′	1.70 *m*	5′	1.72 *m*	1.78 *m*	1.96 *m*	5′	1.70 *m*
		4′	4.60 *br q* (6)	4.75 *dd* (10, 6)	4′	4.30 *m*	6′	4.56 *q* (7)	4.64 *q* (6)	5.48 *br q* (7)	6′	4.30 *m*
					5′	1.70 *m*					7′	1.70 *m*
					6′	4.60 *m*					8′	4.60 *m*
1′	6.27 *dd* (16, 6)	5′	6.21 *dd* (16, 6)	6.30 *dd* (16, 6)	7′	6.20 *dd* (16, 6)	7′	6.22 *dd* (16, 7)	6.26 *dd* (16, 6)	6.11 *dd* (16, 7)	9′	6.20 *dd* (16, 6)
2′	6.73 d (16)	6′	6.59 d (16)	6.64 d (16)	8′	6.60 *d* (16)	8′	6.60 *dd* (16, 1)	6.62 *dd* (16, 1)	6.63 d (16)	10′	6.60 d (16)
HAr	7.30 *m*	HAr	7.30 *m*	7.30 *m*	HAr	7.30 *m*	HAr	7.30 *m*	7.30 *m*	7.50 *m*	HAr	7.30 *m*
							Ac			2.01 *s*		
							Ac			2.07 *s*		

[a] Chemical shifts in ppm (*J* in Hz).

2. Results and discussion

Compounds **1**–**13** were purified as described in Section 3; (+) Goniothalamin (**1**) had been previously isolated from *C. caloneura* (Hlubucek & Robertson, 1967), *C. latifolia* and *C. wyliei* (Drewes et al., 1995) and from *Goniothalamus* species (Jewers et al., 1972).

The ^{1}H- and ^{13}C-NMR spectroscopic signals of the other isolated compounds revealed certain common features, viz. a styryl group and a 5,6-dihydro-α-pyrone group (Tables 1–4). In compounds **2**–**7**, these groups are connected by a linear and hydroxylated carbonic chain, and by a carbonic chain with a dihydroxy-tetrahydropyrane ring in compounds **8**–**13**. In addition, compounds **4**, **5**, **7**, **9**, **11** and **13** have a *trans*-disubstituted double bond at C1′–C2′ [$\sim\delta$ 5.7 *ddt* (J = 16, 6 and 1 Hz) and ~5.9 *dtd* (J = 16, 7 and 1 Hz)]. These skeleta were proposed based on ^{1}H–^{1}H COSY experiments.

The molecular weight of each compound was determined by observation of $[M + K]^+$ and $[M + Na]^+$ adducts in the ES–MS spectra. The hydroxymethine carbons on the aliphatic chains were proposed based on their ^{13}C-NMR chemical shifts (δ 64–74), associated with the strong IR absorption at 3400–3390 cm^{-1} and the fragmentation patterns $[M - H_2O + H]^+$, $[M - H_2O]^+$, $[M - H_2O - H]^+$, $[M - 2H_2O + H]^+$, $[M - 2H_2O]^+$, and/or $[M - 2H_2O - H]^+$ revealed by ES–MS spectral analyses. The diacetates obtained from **5**, **8** and **9** confirmed the presence of these hydroxyl groups.

The ^{1}H-NMR signals of compounds **1**–**7** (Table 1) were assigned by ^{1}H–^{1}H COSY. The ^{13}C-NMR signals of **5** were assigned by ^{1}H–^{13}C COSY, while the signals for compounds **2**, **3** and **4** were assigned by comparison with **5** (Table 2).

Compounds **2** and **3** possess the same molecular formula ($C_{17}H_{20}O_4$) and showed in the ^{1}H- and ^{13}C-NMR spectra, besides absorptions observed for styryl and α-pyrone groups, signals relative to two oxymethine and two methylene carbons. Compound **2** was identified as cryptofolione, previously isolated from *C. latifolia* and *C. myrtifolia* (Sehlapelo, Drewes & Scott-Shaw, 1994). More subtle differences in the ^{13}C-NMR chemical shifts of compounds **2** and **3** were noted at carbons 2′ and 4′ (Table 2), showing that they consist of a diastereomeric pair. To determine the relative configuration of these pairs, compounds **14**–**17** were used as models (Hoffmann & Wiedmann, 1985), and the hydrogen bonding of 1,3-diols was considered to enable the molecule to assume a chair-like conformation (Fig. 1). The lower field chemical shifts of C2′ and C4′ of compound **2** were in concordance with an *erythro* configuration, where the substituents (styryl and α-pyrone ring) possess an equatorial conformation. On the other hand, the higher field chemical

shifts of C2′ and C4′ in the compound **3** point to an *erythro* configuration, where at least one substituent (styryl or pyrone ring) possesses an axial conformation.

Compounds **4** and **5**, with an additional *trans*-vinyl moiety as compared to compounds **2** and **3**, possess a molecular formula $C_{19}H_{22}O_4$, and constitute another pair of 1,3-diols (Table 2). Thus, the lower field chemical shifts of C4′ and C6′ point to an *erythro* configuration for compound **4** and the higher field chemical shifts of C4′ and C6′ indicate a *threo* configuration for compound **5**.

The molecular formula of **6** ($C_{19}H_{24}O_5$) differs from the molecular formula of **7** ($C_{21}H_{26}O_5$) only by a C_2H_2 unit, attributed to a *trans*-vinyl moiety. The relative configurations of three oxymethine carbons of compounds **6** and **7** were established based on comparison of their ^{13}C-NMR chemical shifts with those of compounds **2** or **3** and **4** or **5**, respectively. It was possible to propose a *threo* relationship between OH-2′ and OH-4′ of compound **6** and between OH-4′ and OH-6′ of compound **7** when C2′ (δ 64.5) of **6** was compared with C2′ (δ 64.7) of **3** and when C4′ (δ 68.1) of **7** was compared with C4′ (δ 68.1) of **5**, respectively. Similarly, C6′ (δ 73.8) of compound **6** and C8′ (δ 73.6) of compound **7** were compared with C4′ (δ 73.7) of **2** and C6′ (δ 73.5) of **4**, respectively, indicating an *erythro* relationship between OH-4′ and OH-6′ of **6** and OH-6′ and OH-8′ of **7**.

The ^{1}H–^{1}H COSY correlation spectra and the ^{1}H-NMR coupling constants observed for **8**–**13** are in accordance with a dihydroxy-tetrahydropyrane ring, probably originated by dehydration and cyclization of polyhydroxyalkenyl chain. The diacetates **8a** and **9a** obtained from compounds **8** and **9** confirmed two hydroxyl groups. The assignment of ^{1}H- and ^{13}C-NMR chemical shifts for compounds **8**–**10** and **12**–**13** was carried out by ^{1}H–^{1}H and ^{1}H–^{13}C COSY, and for compound **11** the assignment was based on comparison with spectral data of compounds **12**–**13** (Tables 3 and 4).

The stereochemistry of the dihydroxy-tetrahydropyrane ring of compound **8** was determined by analysis of ^{1}H-NMR coupling constants. The H5′ signal (δ 3.22, *dd*, $J \sim 9$ Hz) indicated a *trans*-diaxial relationship with H6′ and H4′; $H3'_{ax}$ (δ 1.46, *ddd*, $J \sim 12$ Hz) shows, besides geminal coupling, a *trans*-diaxial relationship with H4′ and H2′. Therefore, H2′, H4′, H5′ and H6′ are in axial positions.

For compound **9**, the stereochemistry of dihydroxy-tetrahydropyrane ring was also determined by the ^{1}H-NMR coupling constant of H7′ (δ 3.22, *dd*, $J \sim 9$ Hz) and of $H5'_{ax}$ (δ 1.43, *ddd*, $J \sim 12$ Hz) signals, which indicated the axial position of H4′, H6′, H7′ and H8′.

The H6′ and H8′ signals in the ^{1}H-NMR spectrum of compound **10** are overlapped. However, the contour lines of H6′–H7′ cross-peak in the ^{1}H–^{1}H COSY spectrum were used to determine the multiplicity of H6′ (δ

Table 2
^{13}C-NMR spectral data of compounds **1**–**7** and **5a**, and selected data of **14**–**17** ($CDCl_3$, 50 MHz)[a]

C	1	C	2	3	C	4	5	5a	C	6	C	7
2	163.9	2	164.0	164.5	2	164.0	164.0	164.0	2	164.5	2	164.1
3	121.5	3	121.9	121.3	3	121.6	121.5	121.6	3	121.3	4	121.4
4	144.7	4	145.4	145.5	4	144.7	144.7	144.6	4	145.5	4	144.8
5	29.8	5	29.9	29.7	5	29.7	29.7	29.6	5	29.9	5	29.7
6	77.9	6	74.7	75.0	6	77.2	77.8	77.8	6	75.1	6	77.9
					1′	130.2	129.9	128.0			1′	129.7
					2′	130.8	131.1	130.4			2′	131.4
									1′	42.9	3′	40.3
									2′	64.5	4′	68.1
		1′	42.9	42.4	3′	40.8	40.4	37.6	3′	42.5	5′	42.3
		2′	67.5	64.7	4′	71.2	68.1	68.7	4′	70.2	6′	70.0
		3′	43.5	43.2	5′	42.8	42.2	38.5	5′	43.3	7′	42.9
		4′	73.7	70.5	6′	73.5	70.4	70.7	6′	73.8	8′	73.6
1′	125.6	5′	130.3	130.3	7′	130.0	130.0	129.3	7′	130.3	9′	130.2
2′	133.1	6′	131.5	131.5	8′	131.5	131.7	132.8	8′	131.5	10′	131.6
1″	135.7	1″	136.5	136.5	1″	136.4	136.6	136.0	1″	136.0	1″	136.5
2″/6″	126.6	2″/6″	126.5	126.5	2″/6″	126.5	126.5	126.6	2″/6″	126.6	2″/6″	126.5
3″/5″	128.6	3″/5″	128.6	128.6	3″/5″	128.6	128.6	128.6	3″/5″	128.7	3″/5″	128.6
4″	128.5	4″	127.8	127.8	4″	127.8	127.7	126.9	4″	127.8	4″	127.8
					Ac[b]			21.1				
					Ac[b]			21.1				

[a] The data corresponding to C2′ (C4′) and C4′ (C6′) for compounds **14**–**17**: compound **14**: 67.0 and 66.3; compound **15**: 65.6 and 65.0; compound **16:** 71.7 and 68.6; compound **17:** 68.0 and 65.7.

[b] C═O from acetate units were not observed.

Table 3
^{1}H-NMR data of compounds **8**–**13** and **8a**–**9a**, in $CDCl_3$, 200 MHz[a]

H	**8**	**8a**	**10**	**12**	H	**9**	**9a**	**11**	**13**
3	6.00 *ddd* (10, 2, 1.5)	6.05 *m*	6.01 *dt* (10, 1)	6.03 *ddd* (10, 2, 1.5)	3	6.02 *dt* (10, 2)	6.05 *ddd* (10, 3, 1)	6.04 *dt* (10, 2)	6.04 *dt* (10, 2)
4	6.86 *ddd* (10, 5, 3.5)	6.87 *ddd* (10, 5.5, 3)	6.86 *ddd* (10, 5.5, 3)	6.89 *ddd* (10, 5, 3.5)	4	6.85 *ddd* (10, 4.5, 4)	6.68 *ddd* (10, 4.5, 4)	6.87 *dt* (10, 4)	6.87 *ddd* (10, 4.5, 4)
5	2.35 *m*	2.36 *m*	2.36 *m*	2.32 *dddd* (18, 10, 3, 3) 2.48 *dddd* (18, 6, 5, 1)	5	2.45 *m*	2.45 *m*	2.50 *m*	2.45 *m*
6	4.70 *dddd* (9.5, 9, 6, 3)	4.71 *tdd* (9.5, 6, 3.5)	4.76 *dddd* (10, 9, 5, 3.5)	4.80 *m*	6	4.87 *br q* (7)	4.90 *m*	4.89 *br q* (6.5)	4.91 *br q* (7.5)
					1′	5.65 *ddt* (16, 6.5, 1)	5.70 *m*	5.67 *dd* (16, 6.5)	5.69 *ddt* (16, 7, 1)
					2′	5.87 *dtd* (16, 7, 1)	5.90 *m*	5.89 *dt* (16, 7)	5.90 *dtd* (16, 7, 1)
1′	1.77 *ddd* (14, 9.5, 3) 1.91 *ddd* (14, 9.5, 3)	1.87 *ddd* (14, 9.5, 3)	1.90 *m*	1.91 *m*	3′	2.35 *m*	2.35 *m*	2.30 *m*	2.35 *br t* (6.5)
2′	3.90 *m*	3.96 *m*	4.21 *m*	3.82 *m*	4′	3.57 *dtd* (12, 6.5, 2)	3.64 *m*	3.93 *dtd* (10, 5, 1.5)	3.81 *qui* (2.5)
$3'_{ax}$	1.46 *ddd* (12)	1.56 *ddd* (13, 11)	1.75 *m*	1.58 *ddd* (12)	$5'_{ax}$	1.43 *ddd* (12)	1.54 *ddd* (13, 11)	1.58 *ddd* (12, 12, 5)	1.65 *ddd* (13, 10, 10)
$3'_{eq}$	2.02 *ddd* (12, 5, 2)	2.20 *m*	2.00 *m*	1.80 *m*	$5'_{eq}$	2.03 *ddd* (12, 5, 2)	2.20 *m*	1.98 *ddd* (12, 6, 1.5)	1.82 *ddd* (13, 5, 3)
4′	3.80 *m*	5.07 *ddd* (11, 9.5, 5)	4.21 *m*	3.82 *m*	6′	3.72 *m*	5.06 *ddd* (11, 9.5, 5)	4.20 *m*	3.98 *ddd* (10, 5, 3)
5′	3.22 *dd* (9)	4.89 *dd* (9.5)	3.42 *dd* (9.5, 3)	3.82 *m*	7′	3.22 *dd* (9)	4.87 *dd* (9.5)	3.44 *dd* (9, 3)	3.89 *t* (3)
6′	3.80 *m*	3.96 *td* (9, 1)	4.21 *dd* (9)	4.03 *ddd* (5.5, 1.5, 1.5)	8′	3.74 *ddd* (9, 7, 1)	3.92 *ddd* (9.5, 8, 1)	4.20 *dd* (9)	4.68 *ddd* (5.5, 3, 2)
7′	6.20 *dd* (16, 6.5)	6.02 *dd* (16, 7.5)	6.21 *dd* (16, 7)	6.27 *dd* (16, 5.5)	9′	6.21 *dd* (16, 7)	6.05 *dd* (16, 7.5)	6.17 *dd* (16, 7.5)	6.20 *dd* (16, 5.5)
8′	6.68 *d* (16)	6.62 *d* (16)	6.71 *d* (16)	6.70 *dd* (16, 1.5)	10′	6.69 *d* (16)	6.63 *d* (16)	6.72 *d* (16)	6.64 *dd* (16, 2)
HAr	7.33 *m*	7.35 *m*	7.34 *m*	7.33 *m*	HAr	7.32 *m*	7.35 *m*	7.34 *m*	7.35 *m*
Ac		1.95 *s*			Ac		1.95 *s*		
Ac		2.04 *s*			Ac		2.04 *s*		

[a] Chemical shifts in ppm (J in Hz).

Table 4
^{13}C-NMR data of compounds **8**–**13**, **8a** and **9a** ($CDCl_3$, 50 MHz)

C	8a	8	10	12	C	9a	9	11	13
2	Not observed	164.5	164.0	164.3	2	Not observed	164.0	Not observed	164.0
3	121.4	121.3	121.4	121.4	3	121.6	121.6	121.5	121.6
4	145.0	145.2	145.1	145.1	4	144.6	144.7	144.7	144.6
5	29.8	29.8	30.0	29.9	5	29.7	29.7	29.7	28.8
6	74.2	74.4	74.9	74.3	6	77.9	77.9	77.1	77.0
					1′	129.9	129.5	129.2	129.6
					2′	130.2	130.9	131.2	131.0
1′	40.9[a]	41.1	41.1	41.3	3′	38.1	38.3[a]	38.2	37.2
2′	70.6[a]	70.7	67.1[a]	69.4[a]	4′	74.4[a]	74.7	70.5	68.3
3′	37.0[a]	39.0	38.1	35.2	5′	36.1	38.2[a]	37.0	33.6
4′	71.6[a]	72.3	66.8[a]	70.3[a]	6′	71.8[a]	72.5	66.8	65.2
5′	72.5[a]	75.9	71.3	71.0[a]	7′	72.5[a]	75.9	71.3	69.7
6′	79.4	80.2	76.5	78.4	8′	79.6	80.6	76.8	76.1
7′	125.1	126.1	126.9	125.8	9′	125.1	126.1	126.9	124.9
8′	134.5	133.5	133.8	132.3	10′	134.5	133.8	133.8	133.6
1″	Not observed	136.3	136.0	136.5	1″	Not observed	136.2	Not observed	136.1
2″/6″	126.7	126.6	126.6	126.5	2″/6″	126.7	126.7	126.7	126.5
3″/5″	128.3	128.5	128.6	128.6	3″/5″	128.6	128.6	128.6	128.7
4″	128.1	128.0	128.0	127.9	4″	128.1	128.0	128.0	128.2
Ac[b]	21.0				Ac[b]	21.1			21.1
Ac[b]	20.8				Ac[b]	20.9			21.1

[a] Values with same letter can be interchangeable in the same column.
[b] Only Me from acetate units were observed in ^{13}C-NMR spectrum.

4.21, *dd*, $J \sim 9$ Hz), showing the axial positions of H6′ and H5′, and the multiplicity of H5′ (*dd*, J = 9.5 and 3 Hz), which defined the equatorial position of H4′. The position of H2′ can not be determined by ^{1}H-NMR spectroscopy. However, comparison of the diamagnetic shift observed on α, β and γ carbons, when the hydroxyl group on C4′ (**8** and **10**) or on C6′ (**9** and **11**) changes from an equatorial to an axial position, confirms the same configuration of the tetrahydropyrane rings in compounds **8**/**9** and **10**/**11**, respectively.

The configuration of compound **11** was determined in a similar way. The contour lines of H8′–H9′ cross-peak observed in the ^{1}H–^{1}H COSY spectrum showed that H8′ is a double doublet ($J \sim 9$ Hz), allowing the assignment of the axial position to H8′ and H7′. Therefore, H6′ is in an equatorial position because H7′ signal is a double doublet (J = 9 and 3 Hz). The axial position of H4′ was determined through the multiplicity of $H5'_{ax}$ (δ 1.58, *ddd*, $J \sim 12$, 12 and 5 Hz), which can be explained by the geminal coupling $H5'_{ax}$–$H5'_{eq}$ (J = 12 Hz), *trans*-diaxial coupling $H5'_{ax}$–$H4'_{ax}$ (J = 12 Hz) and $H5'_{ax}$–$H6'_{eq}$ (J = 5 Hz).

In compound **12**, the multiplicity of $H3'_{ax}$ (δ 1.58, *ddd*, $J \sim 12$ Hz) points to axial position of H2′ and H4′, and the coupling constant of 1 Hz observed in $H3'_{eq}$ (δ 1.68, *dddd*, J = 13, 5, 2.5 and 1 Hz) in ^{1}H-NMR spectra in CD_3CN, results from a long range W coupling constant between $H3'_{eq}$ and $H5'_{eq}$. The signal of H6′ (δ 4.03, ddd, J = 5.5, 1.5 and 1.5 Hz, in CD_3CN) does not allow establishment of the stereochemistry at C6′.

For compound **13**, the axial position of H4′ and H6′ was determined by the $H5'_{ax}$ signal (δ 1.65, *ddd*, $J \sim 13$, 10 and 10 Hz), and the equatorial position of H7′ was deduced from the multiplicity of H6′ (δ 3.98, *ddd*, J = 10, 5 and 3 Hz). The resonance of H8′ (δ 4.68, *ddd*, J = 5.5, 3 and 2 Hz), as in the case of H6′ in compound **12**, does not indicate the configuration at C8′.

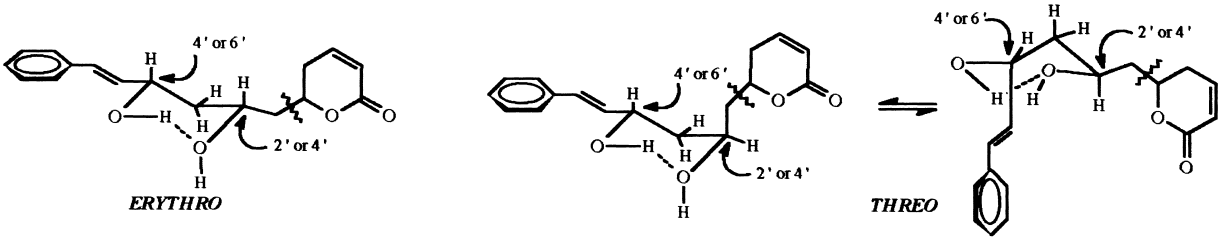
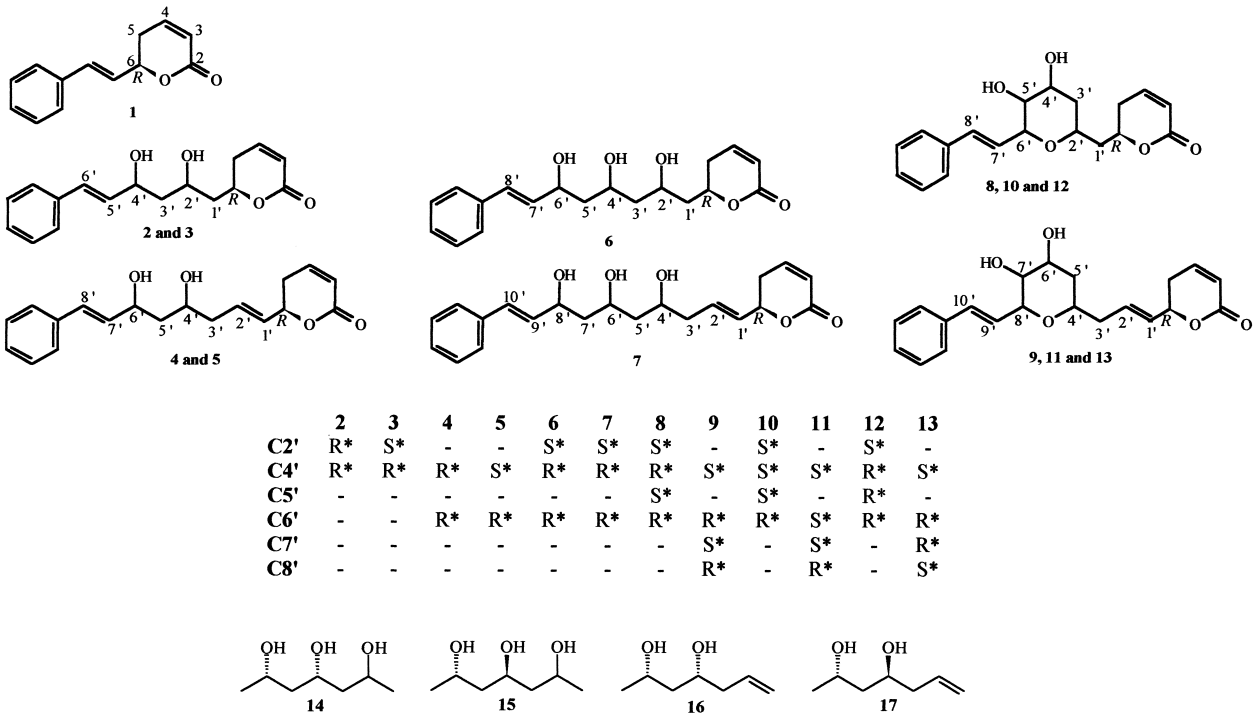


Fig. 1. Chair-like conformation of *erytho* and *threo* 1,3-diols **2**–**5**.



	2	3	4	5	6	7	8	9	10	11	12	13
C2'	R*	S*	-	-	S*	S*	S*	-	S*	-	S*	-
C4'	R*	R*	R*	S*	R*	R*	R*	S*	S*	S*	R*	S*
C5'	-	-	-	-	-	-	S*	-	S*	-	R*	-
C6'	-	-	R*	R*	R*	R*	R*	R*	R*	S*	R*	R*
C7'	-	-	-	-	-	-	-	S*	-	S*	-	R*
C8'	-	-	-	-	-	-	-	R*	-	R*	-	S*

However, C6′ of **12** (δ 78.4) is less shielded than C8′ of **13** (δ 76.1), and it is possible to propose an equatorial position for the styryl moiety on compound **12** and an axial position on compound **13**. This is reinforced by the chemical shifts of H6′ and H8′, δ 4.11 and δ 4.68, respectively, in the ^{1}H-NMR spectra of **12** and **13**.

The C6 *R* configuration of compounds **2**–**13** was determined using the Snatzke rule (Snatzke, 1968), considering the *pseudo-equatorial* orientation of the C6 substituent and the positive signal of the Cotton effect in CD curves at 254–272 nm, due to $n\rightarrow\pi^*$ transition, for all compounds. The conformation of α-pyrone ring was inferred by steric factors (Davies-Coleman & Rivett, 1989) and reinforced by the $H5_{pseudo\text{-}ax}$-NMR signal (δ 2.32, *dddd*, J = 18, 10, 3 and 3 Hz) of compound **12**, which shows a *trans*-diaxial H5–H6 coupling constant (J = 10 Hz) and by the H6-NMR signal of compounds **4**, **5**, **7**, **9**, **11** and **13** (δ 4.9, *ddd*, J = 9, 6 and 6 Hz), in CD_3CN (data not shown), which show *trans*-diaxial H5–H6 coupling constants (J = 9 Hz).

3. Experimental

3.1. Plant material

Branch and stem bark of *C. moschata* were collected at Parque Estadual da Cantareira, São Paulo — SP, Brasil, in April 1989 and November 1991, respectively. The botanical material was identified by Dr. João Batista Baitello from the Instituto Florestal de São Paulo. A voucher specimen is deposited in Herbário Dom Bento Pickel (SPSF 8074).

3.2. General

The silica gel and solvents used for either VLC or flash chromatography were obtained from Merck, whereas the solvents used for HPLC were from either Merck (Lichrosolv grade) or Aldrich (HPLC grade). The HPLC used for analytical analyses was a quaternary pump system Perkin–Elmer Series 4, equipped with a UV/VIS HP 1050 detector and Perkin–Elmer 3600 Data Station; for preparative analyses, a binary pump system (Perkin–Elmer Series 3B) was employed, equipped with a UV/VIS Perkin–Elmer LC-85B detector and an HP 3396 integrator. The ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50 MHz) spectra were recorded on a Bruker-AC 200, using either $CDCl_3$ or CD_3CN (Aldrich) as solvent, with TMS as internal standard.

The elemental analyses were measured on a Elemental Analyser Perkin–Elmer model 2400 CHN. EI–MS data was obtained at 70 eV using a Hewlett Packard HP 5988-A mass spectrometer, and ES–MS data was collected on a Fisons VG Platform II in the positive mode. UV spectra were recorded on a Perkin–Elmer λ 3B Spectrometer; infra-red spectra were obtained with a Nicolet FT 510 Spectrometer. CD curves were obtained using a ISA Jobin Yvon CD 6 dicrograph.

3.3. Extraction and isolation of constituents

Branch bark (197 g) and stem bark (360 g) were individually dried at 50°C, then milled, and each extracted with EtOH–H_2O (96:4 v/v) at room temperature. The EtOH extracts were separately concentrated in vacuo and then partitioned between petrol/EtOH/H_2O (5:3:2 v/v) (3×) and $CHCl_3$/EtOH/H_2O (5:3:2 v/v) (3×). The $CHCl_3$ phase of the branch bark solubles was concentrated in vacuo yielding 5.0 g, and then divided into four fractions (I — 400 mg, II — 900 mg, III — 600 mg, IV — 3000 mg) by VLC (Si-60, 10 × 4.7 cm, 63–200 μm), using a gradient of increasing polarity (petrol/CH_2Cl_2/$CHCl_3$/MeOH 76:10:8:6 to petrol/CH_2Cl_2/$CHCl_3$/MeOH 21:33:25:21). Fraction II was fractionated by VLC (Si-60, 10 × 3.4 cm, 63–200 μm) with the same eluents, yielding IIa (380 mg) and IIb (500 mg). Fraction IIa was then purified by HPLC (Lichrosorb Si-60 250 × 10 mm, 7 μm), with petrol/CH_2Cl_2/$CHCl_3$/MeOH 94:2.5:2:1.5, 5.0 ml/min (280 nm), to give 20 mg of goniothalamin (**1**). Fraction III gave IIIa (210 mg), IIIb (73 mg) and IIIc (85 mg) by flash chromatography (Si-60, 15 × 3 cm, 40–63 μm) eluting with petrol/CH_2Cl_2/$CHCl_3$/MeOH 68.5:13:10:8.5. Fraction IIIc was purified on HPLC (Perkin–Elmer RP-8 250 × 22 mm, 10 μm), eluted with THF/HOAc 5% 19:81, 17 ml/min (250 nm) yielding 5.8 mg of **6** and 7.9 mg of **7**. The $CHCl_3$ phase of stem bark was concentrated in vacuo yielding 10.6 g, and then separated into five fractions (I′ — 25 mg, II′ — 934 mg, III′ — 3000 mg, IV′ — 3500 mg, V′ — 600 mg) by VLC (Si-60, 10 × 8 cm, 63 –200 μm), using a gradient of increasing polarity (CH_2Cl_2 to MeOH). Flash chromatography (Si-60, 15 × 2.5 cm) of fraction II′, eluted with CH_2Cl_2/Et_2O/MeOH 48:48:4, yielded eight fractions (II'_a — 200 mg, II'_b — 47 mg, II'_c — 58 mg, II'_d — 45 mg, II'_e — 47 mg, II'_f — 37 mg, II'_g — 30 mg, II'_h — 415 mg). Fractions II'_b–II'_g, separately, were purified by HPLC (Perkin–Elmer RP-8 250 × 22 mm, 10 μm), eluted with MeOH/H_2O 45:55, 8 ml/min, 270 nm. Fraction II'_b yielded, in order of elution, compounds **4**, **5** and **11**; fraction II'_c yielded **2**, **3**, **10**, **4**, **5** and **11**; fraction II'_d yielded **2**, **3**, **10**, **5** and **9**; fraction II'_e yielded **12**, **8** and **9**; fraction II'_f yielded **12**, **8**, **13** and **9**; and fraction II'_g yielded **12**, **8** and **13**. The total amount obtained of each compound was 2.9 mg of cryptofolione (**2**), 5.8 mg of (**3**), 4.5 mg of (**4**), 13.3 mg of (**5**), 12.0 mg of (**8**), 12.9 mg of (**9**), 5.7 mg of (**10**), 4.4 mg of (**11**), 6.0 mg of (**12**) and 2.5 mg of (**13**).

3.4. Acetylation of **5**, **8** and **9**

100 μl of pyridine and 100 μl of acetic anhydride were added to 2 mg of each compound. After standing overnight at room temperature, the reaction mixture was dried with N_2. The residue was dissolved in $CDCl_3$ for NMR experiments.

3.4.1. Goniothalamin (*1*)

White crystal, mp 85°C, $C_{13}H_{12}O_2$; $\Delta\varepsilon_{max}$ (255 nm) = 5.1 (MeOH *c* 0.2); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1716, 1381, 1245, 1055, 1021, 969, 818, 751, 693; UV λ_{max}^{MeOH} nm (log ε): 210 (5.05), 258 (5.03), 300 (3.95), 310 (3.71); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 201 $[M + H]^+$ (100), 223 $[M + Na]^+$ (75), 239 $[M + K]^+$ (20); ^{1}H- and ^{13}C-NMR spectral data, see Tables 1 and 2, respectively.

3.4.2. Cryptofolione (*2*)

Brown oil, $C_{17}H_{20}O_4$; $\Delta\varepsilon_{max}$ (260 nm) = 2.5 (MeOH, *c* 2.0); UV λ_{max}^{MeOH} nm (log ε): 205 (4.15), 250 (3.78), 282 (3.38), 291 (3.37); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 327 $[M + K]^+$ (98), 311 $[M + Na]^+$ (86), 287 $[M - H]^+$ (13), 271 $[M - H_2O + H]^+$ (3), 269 $[M - H_2O - H]$ (6), 253 $[M - 2H_2O + H]^+$ (6); ^{1}H- and ^{13}C-NMR spectral data, see Tables 1 and 2, respectively.

3.4.3. Cryptomoscatone D2: (6R)-5,6-dihydro-6-[(2′R*,4′R*,5′E)-2′,4′-dihydroxy-6′-phenyl-5′-hexenyl]-2-pyrone (*3*)

Brown oil, $C_{17}H_{20}O_4$, $\Delta\varepsilon_{max}$ (266 nm) = 1.6 (MeOH, *c* 2.0); UV λ_{max}^{MeOH} nm (log ε): 205 (4.26), 249 (4.06), 281 (3.27), 290 (3.20); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 327 $[M + K]^+$ (90), 311 $[M + Na]^+$ (100), 287 $[M - H]^+$ (20), 271 $[M - H_2O + H]^+$ (10), 253 $[M - 2H_2O + H]^+$ (8); ^{1}H- and ^{13}C-NMR spectral data, Tables 1 and 2, respectively.

3.4.4. Cryptomoscatone E1: (6R)-5,6-dihydro-6-[(4′R*,6′R*,1′E,7′E)-4′,6′-dihydroxy-8′-phenyl-1′,7′-octadienyl]-2-pyrone (*4*)

Brown oil, $C_{19}H_{22}O_4$ (calc. 72.61% C, 7.01% H; obs. 72.67% C, 7.04% H); $\Delta\varepsilon_{max}$ (254 nm) = 3.7 (MeOH, *c* 0.5); UV λ_{max}^{MeOH} nm (log ε): 206 (4.29), 250 (4.05), 281 (3.38), 291 (3.33); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 337 $[M + Na]^+$ (100), 313 $[M - H]^+$ (10), 297 $[M - H_2O + H]^+$ (10), 296 $[M - H_2O]^+$ (3), 295 $[M - H_2O - H]^+$ (18), 277 $[M - 2H_2O - H]^+$ (25). ^{1}H- and ^{13}C- NMR spectral data, see Tables 1 and 2, respectively.

3.4.5. Cryptomoscatone E2: (6R)-5,6-dihydro-6-[(4′S*,6′R*,1′E,7′E)-4′,6′-dihydroxy-8′-phenyl-1′,7′-octadienyl]-2-pyrone (*5*)

Brown oil; $C_{19}H_{22}O_4$ (calc. 72.61% C, 7.01% H; obs. 72.24% C, 6.99% H); $\Delta\varepsilon_{max}$ (259 nm) = 3.0 (MeOH, *c* 0.5); UV λ_{max}^{MeOH} nm (log ε): 206 (4.33), 251 (4.12), 283 (3.41), 291 (3.34); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 337 $[M + Na]^+$ (100), 315 $[M + H]^+$ (25), 314 $[M]^+$ (15), 313 $[M - H]^+$ (40), 297

$[M - H_2O + H]^+$ (50), 296 $[M - H_2O]^+$ (10), 295 $[M - H_2O - H]^+$ (40), 279 $[M - 2H_2O + H]^+$ (75), 278 $[M - 2H_2O]^+$ (15), 277 $[M - 2H_2O - H]^+$ (25); ^{1}H- and ^{13}C-NMR spectral data, see Tables 1 and 2, respectively.

*3.4.6. Cryptomoscatone E2 diacetate (**5a**)*

Brown oil, $C_{23}H_{26}O_6$ (calc. 69.35% C, 6.53% H; obs. 69.04% C, 6.57% H); $\Delta\varepsilon_{max}$ (258 nm) = 7.0 (MeOH, *c* 0.5). UV λ_{max}^{MeOH} nm (log ε): 204 (4.35), 249 (4.11), 281 (3.29), 290 (3.19); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 437 $[M + K]^+$ (13), 422 $[M + Na + H]^+$ (25), 421 $[M + Na]^+$ (100), 280 $[M - 2 OAc]^+$ (13), 279 $[M - 2 HOAc + H]^+$ (76). ^{1}H- and ^{13}C-NMR: spectral data, see Tables 1 and 2, respectively.

3.4.7. Cryptomoscatone E3: 5,6-dihydro-6-[(2′S,4′R*,6′R*,7′E)-2′,4′,6′-trihydroxy-8′-phenyl-7′-octenyl]-2-pyrone (**6**)*

Brown oil, $C_{19}H_{24}O_5$; $\Delta\varepsilon_{max}$ (265 nm) = 1.9 (MeOH, *c* 2.0); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3392, 2924, 2856, 1709, 1446, 1443, 1390, 1317, 1257, 1180, 1152, 1115, 1058, 969, 813, 753, 697; UV λ_{max}^{MeOH} nm: 205, 248, 281, 291; EIMS 70 eV, *m/z* (rel. int.): 332 $[M]^+$ (0), 314 $[M - H_2O]^+$ (1), 296 $[M - 2 H_2O]^+$ (10), 278 $[M - 3 H_2O]^+$ (2); ^{1}H- and ^{13}C-NMR: spectral data, see Tables 1 and 2, respectively.

3.4.8. Cryptomoscatone F1: 5,6-dihydro-6-[(4′S,6′R*,8′R*,1′E,9′E)-4′,6′,8′-trihydroxy-10′-phenyl-1′,9′-decadienyl]-2-pyrone (7)*

Brown oil, $C_{21}H_{26}O_5$; $\Delta\varepsilon_{max}$ (260 nm) = 3.0 (MeOH, *c* 0.5). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 2924, 2856, 1709, 1445, 1421, 1386, 1314, 1294, 1252, 1117, 1057, 1020, 970, 819, 752, 697; λ_{max}^{MeOH}; UV nm: 205, 250, 282, 290; EIMS 70 eV, *m/z* (rel. int.): 358 $[M]^+$ (0), 340 $[M - H_2O]^+$ (1), 322 $[M - 2H_2O]^+$ (1), 304 $[M - 3H_2O]^+$ (1). ^{1}H- and ^{13}C-NMR spectral data, see Tables 1 and 2, respectively.

3.4.9. Cryptopyranmoscatone A1: (6R)-5,6-dihydro-6-[(2′S,4′R*,5′S*,6′R*,7′E)-2′,6′-epoxy-4′,5′-dihydroxy-8′-phenyl-7′-octenyl]-2-pyrone (**8**)*

Brown oil, $C_{19}H_{22}O_5$ (calc. 69.09% C, 6.67% H; obs. 68.69% C, 6.64% H); $\Delta\varepsilon_{max}$ (269 nm) = 1.6 (MeOH, *c* 1.0); UV λ_{max}^{MeOH} nm (log ε): 209 (4.42), 251 (4.27), 281 (3.68), 290 (3.19); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 369 $[M + K]^+$ (50), 353 $[M + Na]^+$ (100), 329 $[M - H]^+$ (8), 311 $[M - H_2O - H]^+$ (12), 295 $[M - 2H_2O + H]^+$ (12); ^{1}H- and ^{13}C-NMR spectral data, see Tables 3 and 4, respectively.

*3.4.10. Cryptopyranmoscatone A1 diacetate (**8a**)*

Brown oil, $C_{23}H_{26}O_7$ (calc. 66.67% C, 6.28% H; obs. 66.34% C, 6.25% H); $\Delta\varepsilon_{max}$ (248 nm) = 4.0 (MeOH, *c* 1.0); λ_{max}^{MeOH} UV nm (log ε): 205 (4.31), 250 (4.02), 281 (3.24), 291 (3.24); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 437 $[M + Na]^+$ (100), 295 $[M - 2 HOAc + H]^+$ (10), 293 $[M - 2HOAc - H]^+$ (5); ^{1}H- and ^{13}C-NMR spectral data, see Tables 3 and 4, respectively.

3.4.11. Cryptopyranmoscatone B1: (6R)-5,6-dihydro-6-[(4′S,6′R*,7′S*,8′R*,1′E,9′E)-4′,8′-epoxy-6′,7′-dihydroxy-10′-phenyl-1′,9′-decadienyl]-2-pyrone (**9**)*

Brown oil; $C_{21}H_{24}O_5$; $\Delta\varepsilon_{max}$ (269 nm) = 1.1 (MeOH, *c* 0.5); UV λ_{max}^{MeOH} nm (log ε): 204 (4.26), 251 (3.93), 280 (3.56), 289 (3.54); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 395 $[M + K]^+$ (80), 379 $[M + Na]^+$ (100), 355 $[M - H]^+$ (10), 339 $[M - H_2O + H]^+$ (5), 337 $[M - H_2O - H]^+$ (20), 321 $[M - 2H_2O + H]^+$ (10), 319 $[M - 2H_2O - H]^+$ (5); ^{1}H- and ^{13}C-NMR spectral data, see Tables 3 and 4, respectively.

*3.4.12. Cryptopyranmoscatone B1 diacetate (**9a**)*

Brown oil; $\Delta\varepsilon_{max}$ (269 nm) = 1.1 (MeOH, *c* 0.5); UV λ_{max}^{MeOH} nm (log ε): 204 (4.33), 250 (4.01), 280 (3.52), 291 (3.40); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 479 $[M + K]^+$ (40), 463 $[M + Na]^+$ (100); ^{1}H - and ^{13}C-NMR spectral data, see Tables 3 and 4, respectively.

3.4.13. Cryptopyranmoscatone A2: (6R)-5,6-dihydro-6-[(4′S,6′S*,7′S*,8′R*,1′E,9′E)-2′,6′-epoxy-4′,5′-dihydroxy-8′-phenyl-7′-octenyl]-2-pyrone (**10**)*

Brown oil, $C_{19}H_{22}O_5$; $\Delta\varepsilon_{max}$ (268 nm) = 1.4 (MeOH, *c* 1.0); UV λ_{max}^{MeOH} nm (log ε): 204 (4.17), 248 (3.83), 280 (3.16), 290 (3.00); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 369 $[M + K]^+$ (60), 353 $[M + Na]^+$ (100), 313 $[M - H_2O + H]^+$ (10), 311 $[M - H_2O - H]^+$ (8), 295 $[M - 2H_2O + H]^+$ (90). ^{1}H- and ^{13}C-NMR spectral data, see Tables 3 and 4, respectively.

3.4.14. Cryptopyranmoscatone B2: (6R)-5,6-dihydro-6-[(2′S,4′S*,5′S*,6′R*,7′E)-4′,8′-epoxy-6′,7′-dihydroxy-10′-phenyl-1′,9′-decadienyl]-2-pyrone (**11**)*

Brown oil, $C_{21}H_{24}O_5$ (calc. 70.79% C, 6.74% H; obs. 70.92% C, 6.77% H); $\Delta\varepsilon_{max}$ (255 nm) = 2.3 (MeOH, *c* 0.5); UV λ_{max}^{MeOH} nm (log ε): 204 (4.02), 250 (3.57), 280 (3.28); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 395 $[M + K]^+$ (100), 379 $[M + Na]^+$ (195), 355 $[M - H]^+$ (10), 339 $[M - H_2O + H]^+$ (5), 337 $[M - H_2O - H]^+$ (15), 321 $[M - 2H_2O + H]^+$ (12), 319 $[M - 2H_2O - H]^+$ (8); ^{1}H- and ^{13}C-NMR spectral data, see Tables 3 and 4, respectively.

3.4.15. Cryptopyranmoscatone A3: (6R)-5,6-dihydro-6-[(2′S,4′R*,5′R*,6′R*,7′E)-2′,6′-epoxy-4′,5′-dihydroxy-8′-phenyl-7′-octenyl]-2-pyrone (**12**)*

Brown oil, $C_{19}H_{22}O_5$; $\Delta\varepsilon_{max}$ (272 nm) = 1.3

(MeOH, *c* 1.0); UV λ_{max}^{MeOH} nm (log ε): 206 (4.35), 248 (4.16), 280 (3.27), 290 (3.09); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 369 $[M + K]^+$ (15), 353 $[M + Na]^+$ (100), 295 $[M - 2H_2O + H]^+$ (10). ^{1}H- and ^{13}C -NMR spectral data, see Tables 3 and 4, respectively.

3.4.16. Cryptopyranmoscatone B4: (6R)-5,6-dihydro-6-[(4′S,6′R*,7′R*,8′S*,1′E,9′E)-4′,8′-epoxy-6′,7′-dihydroxy-10′-phenyl-1′,9′-decadienyl]-2-pyrone (**13**)*

Brown oil, $C_{21}H_{24}O_5$; $\Delta\varepsilon_{max}$ (256 nm) = 3.3 (MeOH, *c* 0.5); UV λ_{max}^{MeOH} nm (log ε): 204 (4.20), 254 (3.83), 280 (3.59); ES–MS, *m/z* (rel. int.) (40 V, positive mode): 395 $[M + K]^+$ (100), 379 $[M + Na]^+$ (90), 355 $[M - H]^+$ (20), 337 $[M - H_2O - H]^+$ (15), 321 $[M - 2H_2O + H]^+$ (25), 319 $[M - 2H_2O - H]^+$ (12). ^{1}H- and ^{13}C-NMR spectral data, see Tables 3 and 4, respectively.

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