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BENZODIOXANE AND β-ARYLOXY-ARYLPROPANE TYPE NEOLIGNANS FROM *LICARIA CHRYSOPHYLLA**

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Key Word Index—*Licaria chrysophylla*; Lauraceae, bark; fruit; eusiderins; virolongins; dihydro-dehydrodiconiferyl alcohol.

Abstract—Bark and fruit calyx of *Licaria chrysophylla* were found to contain five new benzodioxane type neolignans (eusiderins I, J, K, L, M), three new β-aryloxy-arylpropane type neolignans (virolongins E, F, G), besides dihydroconiferyl alcohol and its oxidative dimer dihydro-dehydrodiconiferyl alcohol.

INTRODUCTION

Licaria chrysophylla (Meissn.) Kosterm. (family Lauraceae) has been described as the source of a series of unusual benzofuranoid neolignans [2, 3]. The present report concerns the presence of neolignans belonging to the eusiderin [4–11] and virolongin [1, 8, 12, 13] groups. Thus the bark was found to contain the eusiderins A (**1a**), C (**1c**), I (**1i**), J (**1j**), L (**1l**) and M (**1m**), besides the virolongins B (**2b**), E (**2e**), F (**2f**), G (**2g**); while the fruit calyx was found to contain the eusiderins A (**1a**) and K (**1k**), besides dihydroconiferyl alcohol (**3a**), (2*S*, 3*S*)-dihydro-dehydrodiconiferyl alcohol (**4a**) and the latter's glucoside (**4b**). Compounds **3a**, **4a** and **4b** were separated and identified in the form of their fully acetylated derivatives **3b** (prepared also by synthesis from ferulic acid), **4c** and **4d** [14, 15].

RESULTS

The new neolignans **1i–1m** and **2e–2g** were easily classified into the structural series **1** and **2** by NMR spectral comparisons with the known representatives, respectively **1a–1h** and **2a–2d** (Tables 1–3). For eusiderins, representatives of the *trans* vs *cis* series, **1a**, **1b**, **1e**, **1g–1i**, **1k–1m**, vs **1c**, **1d**, **1j**, are distinguished by ^{1}H NMR (H-7: $\delta 4.5 \pm 0.2/5.1 \pm 0.2$; H-8: $\delta 4.0 \pm 0.2/4.5 \pm 0.2$; $J_{H\text{-}7,\,H\text{-}8} = 8/2$ Hz; H-9: $\delta 1.2 \pm 0.1/1.0 \pm 0.1$) and ^{13}C NMR (C-7: $\delta 80.8 \pm 0.3/77.0 \pm 0.1$; C-8: $\delta 74.0 \pm 0.1/73.1 \pm 0.1$; C-9: $\delta 17.2 \pm 0.2/12.6$) [8, 16]. The characterization of the nature and pattern of the substituents is trival with the exception of the placement of the methoxyl and the aliphatic side chain on the aromatic part of the benzodioxane units. This problem has been solved by the application of the lanthanide induced NMR shift technique for the eusiderins A (**1a**), B (**1b**) [6], C (**1c**) [7], and X-ray crystallography for eusiderin A (**1a**) [9]. No attempt was made to confirm the extension of the validity of the conclusion to the present cases.

DISCUSSION

Airoldi and Merlini [16] have described two model phenyl-methyl-benzodioxanes, one belonging to the *trans*-series (**5a**) and one to the *cis*-series (**5b**). Their absolute configuration is assured by the process of asymmetric synthesis employed. The CD maxima of these compounds show positive signs (Table 4), but differ in wavelength: a red shift is observed upon passing from the *trans* to the *cis* derivative. We have supplied the referred authors with samples and CD curves of another *trans–cis* pair of benzodioxans, eusiderins A and C, both from *Virola pavonis* (DC) Smith (family Myristicaceae) [11]. The red shift between the CD extremes of the two compounds is again clearly noticeable. Upon comparison of our data with those of their model compounds (Table 4) the authors assigned the absolute configuration (7*R*, 8*R*) to eusiderin A and (7*R*, 8*S*) to eusiderin C.

During the present work we again noted a negative sign for the maximum at 242 nm of eusiderin A (**1a**). However, eusiderin I (**1i**) gave a curve of opposite sign and must possess the (7*S*, 8*S*)-configuration. Even more strikingly, eusiderin C from *Licaria chyrsophylla* (**1c**) gave a negative maximum and must thus be enantiomeric to the previously known eusiderin C from *Virola pavonis*. An additional derivative of the *cis*-series, eusiderin J (**1j**) also possesses the (7*S*, 8*R*)-configuration.

We conclude that the *trans*- as well as the *cis*-eusiderins, can appear in two enantiomeric series in the same or in closely related plant species. Accordingly, all previous reports on such compounds will have to be reconsidered in order to check the constancy of optical properties of eusiderins possibly even in different samples of an identical species. Clearly, the CD-correlation with chirality is not applicable to derivatives such as the eusiderins E, G, L and M which display a higher degree of conjugation.

*Part 91 in the series 'The Chemistry of Brazilian Lauraceae'. For Part 90 see ref. [1]. Based in part on the Doctorate theses presented by M. S. da S. and J. M. B.-F. to Universidade de São Paulo (1986).

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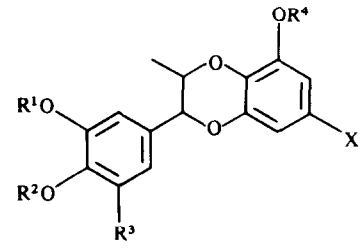
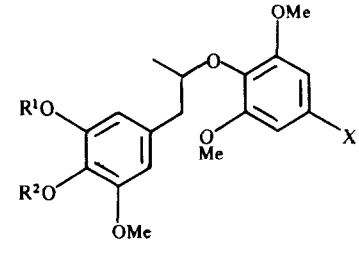


1a *trans*, $R^1 = R^2 = R^4 = Me$, $R^3 = OMe$, $X = CH_2CH{=}CH_2$ [4–9]
1b *trans*, $R^1{-}R^2 = CH_2$, $R^3 = H$, $R^4 = Me$, $X = CH_2CH{=}CH_2$ [6]
1c *cis*, $R^1 = R^2 = R^4 = Me$, $R^3 = OMe$, $X = CH_2CH{=}CH_2$ [7,8]
1d *cis*, $R^1 = R^2 = R^4 = Me$, $R^3 = H$, $X = CH_2CH{=}CH_2$ [7]
1e *trans*, $R^1 = R^4 = Me$, $R^2 = H$, $R^3 = OMe$, $X = CH{=}CHMe$ [8]
1f 7-OH, $R^1 = R^2 = R^4 = Me$, $R^3 = OMe$, $X = CH_2CH{=}CH_2$ [10]
1g *trans*, $R^1 = R^2 = R^4 = Me$, $R^3 = OMe$, $X = CH{=}CHCHO$ [10]
1h *trans*, $R^1 = R^2 = Me$, $R^3 = OMe$, $R^4 = H$, $X = CH_2CH{=}CH_2$ [11]
1i *trans*, $R^1{-}R^2 = CH_2$, $R^3 = OMe$, $R^4 = Me$, $X = CH_2CH{=}CH_2$
1j *cis*, $R^1{-}R^2 = CH_2$, $R^3 = OMe$, $R^4 = Me$, $X = CH_2CH{=}CH_2$
1k *trans*, $R^1 = R^4 = Me$, $R^2 = H$, $R^3 = OMe$, $X = CH_2CH{=}CH_2$
1l *trans*, $R^1 = R^2 = R^4 = Me$, $R^3 = OMe$, $X = CHO$
1m *trans*, $R^1 = R^2 = R^4 = Me$, $R^3 = OMe$, $X = CH{=}CHCH_2OH$

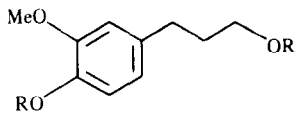


2a $R^1 = R^2 = Me$, $X = CH{=}CHMe$ [1,13]
2b $R^1 = R^2 = Me$, $X = CH_2CH{=}CH_2$ [1,8,12]
2c $R^1{-}R^2 = CH_2$, $X = CH_2CH{=}CH_2$ [8]
2d $R^1 = Me$, $R^2 = H$, $X = CH{=}CHMe$ [8]
2e $R^1 = R^2 = Me$, $X = CH{=}CHCH_2OH$
2f $R^1 = R^2 = Me$, $X = CH{=}CHCHO$
2g $R^1 = R^2 = Me$, $X = CHO$

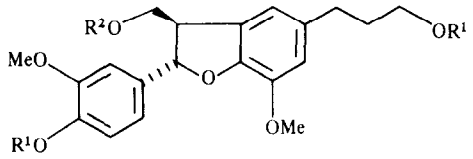
EXPERIMENTAL

Isolation of the constituents. Plant material was collected near Humaitá, Amazonas State, by the late Dr Hipólito P. Ferreira-Filho, UNESP, Araraquara, and classified as stemming from *Licaria chrysophylla* (Meissn.) Kosterm. by Prof. Klaus Kubitzki (Universität Hamburg). Dried powdered bark (1.5 kg) was macerated in EtOH. The soln. was filtered and evapd. The residue (40 g) was partitioned between hexane and 90% aq. MeOH. The MeOH soln was evapd. The residue was dissolved in $CHCl_3$ and filtered through silica gel. The $CHCl_3$ soln. was evapd and the residue (10 g) submitted to silica gel (300 g) CC. Elution with solvent mixtures (C_6H_{14}–EtOAc, EtOAc–EtOH) of increasing polarity gave nine crude fractions, each elaborated further by TLC, flash chromatography or both. The compounds were obtained in the following approx. order: **2b** (215 mg), **2e** (60 mg), **2f** (60 mg), **2g** (10 mg), **1a** (160 mg), **1c** (90 mg), **1i** (110 mg), **1j** (85 mg), chrysophyllin A (100 mg), chrysophyllon IA (165 mg), chrysophyllon IIA (150 mg) [3], **1l** (10 mg), **1m** (10 mg), chrysophyllon III A (80 mg).

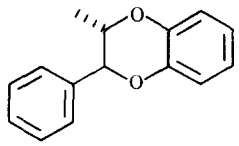
Fresh calyxes (1.5 kg) were macerated in EtOH. The soln was filtered and evapd. The residue (150 g) was partitioned between hexane and 60% aq. EtOH. The hexane soln was evapd and the residue (12.5 g) was suspended in MeOH. The suspension was filtered to eliminate fatty material and the soln evapd. The residue was submitted to silica gel CC. Elution with hexane gave methoxy-γ-asarone (3.5 g) and with C_6H_6 gave sitosterol (150 mg). The EtOH soln was extracted with $CHCl_3$. The $CHCl_3$-layer was separated and evapd. The residue (15.5 g) was submitted to silica gel CC. Elution with hexane–EtOAc (9:1) gave a mixture which was sepd into **1a** (15 mg) and **1k** (8 mg) by TLC (silica gel C_6H_6–EtOAc, 9:1). Elution with C_6H_6–EtOAc 9:1 and 1:1) as well as with C_6H_6–$CHCl_3$ (7:3) gave, in order, the chrisophyllons IIIB, IIA, IIB and IB [3]. Elution with MeOH, acetylation of the product and separation of the mixture by TLC gave, in order, **3b** (5 mg), **4c** (60 mg) and **4d** (135 mg).



3a R = H
3b R = Ac



4a $R^1 = R^2 = H$
4b $R^1 = H$, R^2 = glucosyl
4c $R^1 = R^2$ = Ac
4d R^1 = Ac, R^2 = glucosyltetraacetate



5a β-phenyl *trans*
5b α-phenyl *cis*

Table 1. Comparison of the ^{1}H NMR data (δ, multiplicity, J in Hz) of the known compound **1a** with the new *trans*-eusiderins (**1i**–**1m**) (in $CDCl_3$)

H	**1a** 60 MHz	**1i** 60 MHz	**1j** 60 MHz	**1k** 80 MHz	**1l** 80 MHz	**1m** 300 MHz
2	6.60	6.50	6.56	6.59	6.60	6.58
6	*s*	*s*	*s*	*s*	*s*	*s*
7	4.40	4.40	4.53	4.56	4.55	4.57
	d 8	*d* 8	*d* 8	*d* 8	*d* 8	*d* 8
8	3.8–4.2	3.8–4.1	3.85–4.15	4.1–4.3	3.9–4.3	4.12
	m	*m*	*m*	*m*	*m*	*dq* 8, 6.5
9	1.25	1.20	1.25	1.28	1.25	1.28
	d 6	*d* 7	*d* 6	*d* 7	*d* 6	*d* 6.5
2′	6.40	6.35	6.48			6.60
	d 2	*d* 2	*d* 2	7.13	6.40	*d* 2
6′	6.30	6.25	6.38	*br s*	*br s*	6.68
	d 2	*d* 2	*d* 2			*d* 2
7′	3.25	3.25	3.30	9.8	6.5–6.7	6.54
	d 6	*d* 6	*d* 6	*s*	*m*	*br d* 16
8′	5.7–6.2	5.8–6.2	5.65–6.2	—	6.15–6.4	6.15
	m	*m*	*m*		*m*	*dt* 16, 6.5
9′	4.9–5.2	4.9–5.3	4.9–5.2	—	4.25	4.70
	m	*m*	*m*		*d* 6	*dd* 6.5, 1.5
OMe	3.75	3.80				
	s	*s*				
OMe	3.80	3.90	3.90	3.86–3.88	3.85	3.80–3.90
	s	*s*	*s*		*s*	
OMe		—				
	3.85					
OMe	*s*	—	—	—	—	—
O_2CH_2	—	5.95	—	—	—	—
		s				
OAc	—	—	—	—	—	2.09
						s

Table 2. Comparison of the ^{1}H NMR data (δ, multiplicity, J in Hz) of the known compound **1c** with the new *cis*-eusiderin (**1j**) and of the known compound **2b** with the new virolongins (**2e**–**2g**) (in $CDCl_3$)

	1c 60 MHz	**1j** 60 MHz	**2b** 60 MHz	**2e** 60 MHz	OAc-**2e** 300 MHz	**2f** 300 MHz	**2g** 80 MHz
2	6.50	6.50	6.40	6.50	6.45	6.50	6.40
6	*s*	*s*	*s*	*s*	*s*	*s*	*s*
7	4.95	4.90	2.70	2.70	2.76	2.78	2.70
	d 2	*d* 2	*dd* 14, 8	*dd* 14, 8	*dd* 13.5, 7.5	*dd* 13.5, 7.5	*dd* 14, 8
7	—	—	3.10	3.10	3.12	3.08	3.10
			dd 14, 6	*dd* 14, 6	*dd* 13.5, 5	*dd* 13.5, 6	*dd* 14, 6
8	4.3–4.7	4.3–4.7	4.2–4.6	4.2–4.5	4.42	4.54	4.3–4.6
	m	*m*	*m*	*m*	*m*	*dq* 7.5, 6	*m*
9	1.10	1.10	1.20	1.25	1.24	1.25	1.20
	d 6	*d* 6	*d* 6	*d* 6	*d* 6	*d* 6	*d* 6
2′	6.35	6.40					
	d 2	*d* 2	6.50	6.62	6.61	6.78	7.10
6′	6.25	6.25	*s*	*s*	*s*	*s*	*s*
	d 2	*d* 2					
7′	3.25	3.25	3.30	6.40	6.61	7.40	9.80
	d 6	*d* 6	*d* 7	*d* 7	*dt* 16, 1.5	*d* 15.5	*s*
8′	5.8–6.2	5.6–6.2	5.8–6.3	5.8–6.3	5.77	6.64	—
	m	*m*	*m*	*m*	*dt* 11.5, 6.5	*dd* 15.5, 8	—
9′	4.9–5.2	4.9–5.3	4.95–5.3	4.25	4.86	9.68	—
	m	*m*	*m*	*d* 6	*dd* 6.5, 2	*d* 8	—
OMe	3.75	3.80					
	s	*s*	3.80				
OMe	3.80	3.90	*s*				
	s	*s*					
OMe	3.85	—		3.85	3.80–3.84	3.82–3.85	3.82–3.87
	s			*s*			
OMe		—	3.85				
			s				
OMe	—	—					
O_2CH_2	—	5.90	—	—	—	—	—
		s					
OAc	—	—	—	—	2.09	—	—
					s		

(7*S*,8*S*)-Δ$^{8'}$-5,5′-*Dimethoxy*-3,4-*methylenedioxy*-7.O.3′,8.O.4′-*neolignan* (eusiderin I, **1i**). Oil. UV λ_{max}^{MeOH} nm: 228, 276 (ε 16 150, 5050). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640, 1600 1510, 1460, 1415, 1370, 1235, 1205, 1150, 1105, 1045, 1000, 935, 840. MS *m/z* (rel. int.): 370 [M]$^+$ (28), 328 (4), 205 (5), 193 (12), 192 (100), 191 (14), 178 (2), 165 (3), 150 (6), 135 (2). CD (MeOH; *c* 1.0 mg/25 ml): $[\theta]_{225}$ 0, $[\theta]_{242}+7050$, $[\theta]_{225}$ 0, $[\theta]_{267}-950$, $[\theta]_{290}$ 0.

(7*S*,8*R*)-Δ$^{8'}$-5,5′-*Dimethoxy*-3,4-*methylenedioxy*-7.O.3′,8.O.4′-*neolignan* (eusiderin J, **1j**). Oil. UV λ_{max}^{MeOH} nm: 225, 279 (ε 15 400, 4850). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640, 1600, 1510, 1430, 1220, 1100, 1050, 1020, 970, 940, 830. MS *m/z* (rel. int.): 370 [M]$^+$ (23), 328 (4), 286 (10), 205 (11), 193 (12), 192 (100), 191 (19), 165 (5), 135 (2). CD (MeOH; *c* 1.0 mg/25 ml): $[\theta]_{245}-6100$, $[\theta]_{263}$ 0, $[\theta]_{278}+1665$, $[\theta]_{325}$ 0.

rel-(7*R*,8*R*)-Δ$^{8'}$-4-*Hydroxy*-3,5,5′-*trimethoxy*-7.O.3′,8.O.4′-*neolignan* (eusiderin K, **1k**). Mp 85–87°. UV λ_{max}^{MeOH} nm: 230, 280 (ε 7050, 1850). IR ν_{max}^{KBr} cm^{-1}: 3450, 1595, 1505, 1465, 1345, 1220, 1105, 830. MS *m/z* (rel. int.): 372 [M]$^+$ (19), 194 (100), 181 (5), 167 (8).

rel-(7*R*,8*R*)-3,4,5,5′-*Tetramethoxy*-7′-*oxo*-8′,9′-*bisnor*-7.O.3′,8.O.4′-*neolignan* (eusiderin L, **1l**). Oil, UV λ_{max}^{EtOH} nm: 226, 308 (ε 28 650, 5800). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685, 1590, 1440, 1360, 1325, 1150, 1130, 1100, 1000, 985, 830. MS *m/z* (rel. int.): 374 [M]$^+$ (60), 209 (14), 208 (100), 195 (13), 193 (61), 191 (12), 178 (17), 165 (9), 149 (6), 135 (7). CD (MeOH; 1.0 mg/25 ml): $[\theta]_{230}0$, $[\theta]_{243}-5250$, $[\theta]_{260}$ 0, $[\theta]_{275}-3200$, $[\theta]_{310}$ 0, $[\theta]_{310}-3550$, $[\theta]_{328}$ 0.

rel-(7*R*,8*R*)-Δ$^{7'}$-9′-*Hydroxy*-3,4,5,5′-*tetramethoxy*-7.O.3′,8.O.4′-*neolignan* (eusiderin M, **1m**). Oil. UV λ_{max}^{EtOH} nm: 245, 293 (ε 16 400, 5750). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500, 1660, 1580, 1500, 1460, 1415, 1270, 1235, 1130, 1010, 960, 925. MS *m/z* (rel. int.): 420 [M]$^{+\cdot}$ (0), 387 (3), 372 (2), 208 (100), 193 (60), 179 (8), 165 (9), 150 (5), 135 (6).

Δ$^{7'}$-9′-*Hydroxy*-3,4,5,3′,5′-*pentamethoxy*-8.O.4′-*neolignan* (virolongin E, **2e**). Oil. UV λ_{max}^{EtOH} nm: 248, 295 (ε 15 750, 5100). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 1665, 1580, 1495, 1450, 1325, 1270, 1235, 1180, 1130, 1050, 960, 925. MS *m/z* (rel. int.): 418 [M]$^+$ (2), 224 (3), 210 (13), 209 (100), 208 (12), 194 (11), 193 (10), 181 (19), 179 (10), 167 (10), 165 (5), 154 (6), 149 (17), 135 (5). CD (MeOH; *c* 1.0 mg/25 ml): $[\theta]_{235}+1650$, $[\theta]_{239}$ 0, $[\theta]_{244}-2850$, $[\theta]_{249}$ 0, $[\theta]_{254}+3500$, $[\theta]_{259}$ 0, $[\theta]_{260}-500$, $[\theta]_{262}$ 0, $[\theta]_{265}+1000$, $[\theta]_{267}$ 0, $[\theta]_{268}-1250$, $[\theta]_{271}$ 0, $[\theta]_{276}+2750$, $[\theta]_{278}$ 0, $[\theta]_{280}-350$, $[\theta]_{282}$ 0, $[\theta]_{284}+1250$, $[\theta]_{287}$ 0, $[\theta]_{300}-1150$, $[\theta]_{370}$ 0. *Acetate*. Oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1745, 1675, 1590, 1515, 1505, 1470, 1425, 1380, 1335, 1240, 1180, 1130, 1050, 1010, 970, 930, 760. MS *m/z* (rel. int.): 460 [M]$^+$ (4), 401 (5), 252 (3), 210 (13), 209 (10), 208 (15),

Table 3. Comparison of the ^{13}C NMR data (20 MHz, δ) of *trans*-eusiderins (**1a, 1i, 1k**), *cis*-eusiderins (**1c, 1j**) and virolongins (**2b, 2e, 2f**) (in $CDCl_3$)

C	1a	1i	1k	1c	1j	2b	2e	2f
1	132.4	132.1	132.3	129.6	131.2	134.8	132.1	*
2	104.7	101.4	104.2	103.2	100.3	106.6	106.6	106.7
3	153.6	149.0	147.2	153.5	149.0	153.6	153.7	154.0
4	138.4	137.1	135.4	137.8	137.3	136.5	134.6	*
5	153.6	143.6	147.2	153.5	143.5	153.6	153.7	154.0
6	104.7	107.3	104.2	103.2	106.1	106.6	106.6	106.6
7	81.1	80.6	81.1	77.1	76.9	43.6	43.5	43.6
8	74.1	73.9	74.1	73.2	73.0	79.5	79.6	80.0
9	17.3	17.0	17.1	12.6	12.6	19.6	19.6	19.7
1′	132.6	131.3	132.0	132.5	131.3	134.5	131.0	*
2′	109.7	109.4	109.5	109.8	109.4	105.7	103.7	105.9
3′	144.4	144.1	144.0	143.4	143.2	152.8	152.7	152.9
4′	131.5	131.1	131.7	132.3	132.1	135.3	136.0	*
5′	148.7	148.4	148.0	149.2	149.0	152.8	152.7	152.9
6′	104.8	104.5	102.5	105.1	104.9	105.7	103.7	105.9
7′	40.0	39.7	44.6	40.0	39.9	40.5	131.0	152.5
8′	137.4	137.1	136.8	137.5	137.3	137.2	127.8	127.8
9′	115.8	115.5	115.7	115.9	115.6	115.8	63.4	193.1
OMe	56.0	55.2	56.0	56.1	56.0			
OMe	56.2	55.5	56.3	56.2	56.7	56.0	56.0	56.0
OMe	56.3	—			—			
OMe	60.8	—	—	60.9	—	56.6		
OMe	—	—	—	—	—	60.6	60.6	60.9
O_2CH_2	—	101.4	—	—	101.4	—	—	—

*Undetected.

Table 4. Comparison of CD data of the models **5a** (*trans*) and **5b** (*cis*) and of eusiderins of the *trans* (**1a, 1i**) and *cis* (**1c, 1j**) series

	λ_{max}	$[\theta]$	Configuration	
Model compound (**5a**)	230.5	+14250	*trans*	*S,S*
Eusiderin A ex *Virola pavonis*	242	−7500	*trans*	*R,R*
1a	242	−4000	*trans*	*R,R*
1i	242	+7050	*trans*	*S,S*
Model compound (**5b**)	237.5	+12900	*cis*	*R,S*
Eusiderin C ex *Virola pavonis*	247.5	+6520	*cis*	*R,S*
1c	246	−6750	*cis*	*S,R*
1j	245	−6100	*cis*	*S,R*

193 (11), 178 (9), 163 (5), 149 (17), 133 (10).

$\Delta^{7'}$-*3,4,5,3′,5′-Pentamethoxy-9′-oxo-8.O.4′-neolignan* (virolongin F, **2f**). Oil. UV λ_{max}^{EtOH} nm: 231, 280, 326 (ε 21 350, 4750, 2100). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1675, 1590, 1490, 1450, 1375, 1330, 1130, 1050, 1000, 970, 910. MS *m/z* (rel. int.): 416 $[M]^{+\cdot}$ (1), 224 (2), 209 (7), 208 (4), 181 (5), 179 (3), 167 (19), 149 (51). CD (MeOH; *c* 1.0 mg/25 ml): $[\theta]_{232}$ 0, $[\theta]_{237}$ −3750, $[\theta]_{240}$ 0, $[\theta]_{243}$ +7300, $[\theta]_{250}$ 0, $[\theta]_{294}$ −3550, $[\theta]_{370}$ 0.

3,4,5,3′,5′-Pentamethoxy-7′-oxo-8′,9′-bisnor-8.O.4′-neolignan (virolongin G, **2g**). Oil. UV λ_{max}^{EtOH} nm: 230, 305 (ε 24450, 6700). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685, 1590, 1460, 1380, 1325, 1130, 1050, 1000, 970, 915. MS *m/z* (rel. int.): 390 $[M]^{+\cdot}$ (7), 224 (4), 209 (100), 208 (14), 194 (18), 193 (15), 181 (29), 165 (6), 151 (13), 135 (10). CD (MeOH; *c* 1.0 mg/25 ml): $[\theta]_{227}$ 0, $[\theta]_{236}$ −5650, $[\theta]_{270}$ 0, $[\theta]_{285}$ −1150, $[\theta]_{294}$ 0, $[\theta]_{301}$ +1750, $[\theta]_{360}$ 0.

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