Available online at www.sciencedirect.com

ScienceDirect

Tetrahedron Letters 49 (2008) 3268–3272

Tetrahedron Letters

# Revised structures of phenylphenalene derivatives from *Eichhornia crassipes*

Marina DellaGreca *, Lucio Previtera, Armando Zarrelli

*UdR Napoli 4 of Consortium INCA, Dipartimento di Chimica Organica e Biochimica, Università Federico II, Complesso Universitario Monte Sant'Angelo, Via Cinthia 4, I-80126 Napoli, Italy*

Received 15 February 2008; revised 6 March 2008; accepted 17 March 2008
Available online 19 March 2008

## Abstract

Careful 2D-NMR analyses of phenylphenalenes and dimeric phenylphenalenes isolated from *Eichhornia crassipes* allowed to revise the structure of five of them.

*Keywords:* *Eichhornia crassipes*; Phenylphenalenes; Dimeric phenylphenalenes; Spectroscopic analysis

*Eichhornia crassipes*, commonly known as water hyacinth, is invasive in much of the world where it often jams rivers and lakes with uncounted thousands of tons of floating plant matter.[1] In our search for compounds from aquatic plants, phenylphenalene metabolite derivatives were isolated from the ethyl acetate extract of *E. crassipes* and characterized as methyl ether derivatives obtained by treatment with methanolic $CH_2N_2$.[2] The structures were determined, in previous papers,[2] to be 4,9-dimethoxy-7-phenyl-2,3-dihydro-phenalen-1-olo-*O*-methyl ether, 4,9-dimethoxy-7-(4′-methoxy-phenyl)-2,3-dihydro-phenalen-1-olo-*O*-methyl ether, dimer **4**, dimer **5**, and dimer **7**. However, based on the present detailed spectroscopic analysis, their structures may have to be revised.

Phenylphenalenones represent a class of phenylpropanoid derived natural products that occur in the Musaceae (genera *Musa* and *Ensete*)[3–8] as well as in other plant families such as the Haemodoraceae,[9,10] Pontederiaceae,[2,11,12] and Strelitziaceae.[13] Phenylphenalenones from Musaceae and Haemodoraceae are of special interest because of their potential role as phytoalexins and phytoanticipins.[3–6,14]

The structure of compound **1** was revised using two-dimensional NMR (COSY, NOESY, HSQC, and HMBC) techniques. A molecular formula of $C_{22}H_{22}O_3$ (*m*/*z* obsd 334.1569, calcd 334.1566) was assigned using HR-EIMS. The $^1H$ NMR spectrum (Table 1) of **1** displayed signals corresponding to two *ortho*-coupled aromatic protons ($\delta$ 7.20 and 7.63), five aromatic protons of a monosubstituted phenyl ring ($\delta$ 6.96, 7.11, and 7.17), and one aromatic proton of a pentasubstituted phenyl ring ($\delta$ 7.10, s). The COSY spectrum indicated that the signals located at $\delta$ 2.09, 2.19, 2.48, and 3.12 corresponded to two vicinal methylenes and the first was coupled directly bound to a benzylic methine, whose signal was located at $\delta$ 4.88. Furthermore, the $^1H$ NMR spectrum showed the presence of three methoxyl groups ($\delta$ 3.95, 3.91, and 3.48). The $^{13}C$ NMR spectrum (Table 1) showed 19 signals, that were identified by a DEPT experiment, as three methyls, two methylenes, six methines, and eight quaternary carbons. All the carbons were correlated to the respective protons using an HSQC experiment. The connectivity of these fragments was made by the analysis of the HMBC data that was essential to revise the structure of phenalene **1**. The benzyl proton and the methylene ($\delta$ 2.09 and 2.19) attributed to the H-2 gave cross-peaks with the carbons at $\delta$ 145.6 and 127.8 (C-1′ and C-9a), both the methylenes were correlated to

---

* Corresponding author. Tel.: +39 81 674162; fax: +39 81 674393.
*E-mail address:* dellagre@unina.it (M. DellaGreca).

0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.03.072

Table 1
NMR spectral data of compound **1** in $CDCl_3$

| Position | $\delta_{\mathrm{H}}$[a] | $J$ (Hz) | NOESY | $\delta_{\mathrm{C}}$ | HMBC[b] |
|---|---|---|---|---|---|
| 1 | 4.88 dd | 4.6, 2.5 | 2′/6′ | 38.4 (t)[c,d] | 2, 3, 9, 9a, 9b, 1′, 2′/6′ |
| 2ax | 2.09 dddd | 13.1, 13.1, 4.6, 4.6 | | 29.2 (s) | 1, 3, 3a, 9a, 1′ |
| 2eq | 2.19 dddd | 13.1, 4.6, 2.5, 2.5 | 2′/6′ | | |
| 3ax | 2.48 ddd | 17.0, 13.1, 4.6 | 2′/6′ | 18.1 (s) | 1, 2, 3a, 4, 9b |
| 3eq | 3.12 ddd | 17.0, 4.6, 2.5 | | | |
| 3a | | | | 121.0 (q) | |
| 4 | | | | 151.8 (q) | |
| 5 | 7.20 d | 9.0 | 4-OMe | 112.3 (t) | 3a, 4, 6a |
| 6 | 7.63 d | 9.0 | | 125.1 (t) | 4, 6a, 7 |
| 6a | | | | 126.2* (q) | |
| 7 | 7.10 s | | 8-OMe | 105.7 (t) | 6, 6a, 9, 9b |
| 8 | | | | 150.7 (q) | |
| 9 | | | | 146.1# (q) | |
| 9a | | | | 127.8 (q) | |
| 9b | | | | 126.9* (q) | |
| 1′ | | | | 145.6# (q) | |
| 2′/6′ | 6.96 d | 7.5 | 1, 2eq, 3ax, 9-OMe | 128.0 (t) | 1, 4′ |
| 3′/5′ | 7.17 t | 7.5 | | 128.0 (t) | 1′, 4′ |
| 4′ | 7.11 t | 7.5 | | 125.7 (t) | 2′/6′, 3′/5′ |
| 4-OMe | 3.91 s | | 5 | 56.3 (p) | 4 |
| 8-OMe | 3.95 s | | 7 | 55.4 (p) | 8 |
| 9-OMe | 3.48 s | | 2′/6′ | 60.7 (p) | 9 |

[a] $^1$H chemical shift values ($\delta$ ppm from $SiMe_4$) followed by multiplicity and then the coupling constants ($J$ in Hz).

[b] HMBC correlations from H to C.

[c] Letters, p, s, t and q, in parentheses indicate, respectively, the primary, secondary, tertiary, and quaternary carbons, assigned by DEPT.

[d] Values with same superscript were exchangeable.

the carbon at $\delta$ 121.0 (C-3a). The H-3 protons were also correlated to the carbons at $\delta$ 151.8 and 126.9 (C-4 and C-9b). Besides the already-reported correlations, the H-5 and H-6 protons were correlated to the C-4 and C-6a ($\delta$ 126.2) carbons. Finally, the H-7 proton was correlated to the carbons at $\delta$ 125.1 and 146.1, (C-6 and C-9) and to C-6a, C-9b.

The conformation of **1** was determined by the coupling constants of the aliphatic part and from the observed NOESY cross-peak. The pseudo equatorial orientation of H-1 was established by the coupling constants (4.6, 2.5 Hz), and the trans-axial coupling constant of H-2ax with H-3ax (13.1 Hz) indicated a pseudo-chair conformation of this ring. Consistently with these observations, H-2′/6′ showed NOE interactions with the H-2eq and H-3ax indicating that these protons are oriented to the same side of the monosubstituted phenyl ring. Furthermore, the pseudo equatorial orientation of H-1 was confirmed by a NOE cross-peaks of this proton and 9-OMe. Additional NOE cross-peaks were observed for H-5 and H-7 with the methoxyl groups at C-4 and C-8, respectively. Therefore, the revised structure of compound **1** was determined as 4,8,9-trimethoxy-1-phenyl-2,3-dihydro-1*H*-phenalene. Phenylphenalene **1** had an $[\alpha]_{\mathrm{D}}^{20}$ +52 and the CD spectrum showed $[\theta]_{346.0}$ −24 700, $[\theta]_{311.0}$ 6100, $[\theta]_{297.0}$ −3800, $[\theta]_{274.0}$ +21 900. These data compared with that of a similar known compound[12] reasonably indicated a *S* configuration at C-1.

Compound **2** had in the HR-EIMS spectrum a molecular ion peak at $m/z$ 364.1672 and showed 21 carbon signals in the $^{13}$C NMR spectrum[15] consistent with a molecular formula $C_{23}H_{24}O_4$. The $^1$H NMR spectrum[15] showed seven aromatic protons, four methoxyls, two methylenes, and a benzylic methine. These data resembled those of phenalene **1** except for the presence of an additional methoxyl group. Accordingly to the structure, in a NOESY experiment the methoxyl ($\delta$ 3.73) had relation with the broad doublet at $\delta$ 6.72 assigned to the H-3′/H-5′ protons. Therefore, the revised structure of compound **2** was determined as 4,8,9-trimethoxy-1-(4′-methoxyphenyl)-2,3-dihydro-1*H*-phenalene. Phenylphenalene **2** had an $[\alpha]_{\mathrm{D}}^{20}$ +49 and the CD spectrum showed $[\theta]_{350.0}$ −22 000, $[\theta]_{308.0}$ 5000, $[\theta]_{300.0}$ −4000, $[\theta]_{282.0}$ +19 000, indicating the same configuration of phenylphenalene **1** at C-1.

The structure of compound **3** was revised using two-dimensional NMR (COSY, NOESY, HSQC, and HMBC) techniques. A molecular formula of $C_{44}H_{42}O_6$ ($m/z$ obsd 667.2979 $[M+H]^+$, calcd 667.2981) was assigned using HR-MALDI-MS. The $^1$H NMR spectrum (Table 2) of **3** displayed signals corresponding to two *ortho*-coupled aromatic protons ($\delta$ 7.04 and 7.07) and five aromatic protons of a monosubstituted phenyl ring ($\delta$ 7.10, 7.20, and 7.29). Furthermore, the spectrum showed the H-1 benzyl proton ($\delta$ 4.98), the H-2 methylene ($\delta$ 2.30, m), and the H-3 methylene as two double–double doublets at $\delta$ 3.16 and 2.57. Finally, the $^1$H NMR spectrum showed the presence of three methoxyl groups ($\delta$ 3.86, 3.65, and 3.62). The $^{13}$C NMR spectrum (Table 2) showed only 18 signals that were identified by a DEPT experiment, as three methyls, two methylenes, five methines, and eight quaternary carbons.

Table 2
NMR spectral data of compound **3** in $CDCl_3$

| Position | $\delta_H$[a] | $J$ (Hz) | NOESY[b] | $\delta_C$ | HMBC[b,c] |
|---|---|---|---|---|---|
| 1/1″ | 4.98 dd | 4.6, 2.5 | 9-OMe, 2′/6′ | 38.9 (t)[d,e] | 2, 3, 9a, 9b, 1′, 2′/6′ |
| 2/2″ | 2.30 | | 2′/6′ | 29.3 (s) | 1, 3, 3a, 9a, 1′ |
| 3ax/3″ax | 2.57 ddd | 16.8, 12.8, 4.8 | 2′/6′ | 18.4 (s) | 1, 2, 3a, 4, 9b |
| 3eq/3″eq | 3.16 ddd | 16.8, 4.8, 2.4 | | | |
| 3a/3a″ | | | | 120.7 (q) | |
| 4/4″ | | | | 152.5 (q) | |
| 5/5″ | 7.04 d | 9.0 | 4-OMe | 112.1 (t) | 3a, 4, 6a |
| 6/6″ | 7.07 d | 9.0 | | 124.7 (t) | 4, 6a, 7 |
| 6a/6a″ | | | | 125.0 (q) | |
| 7/7″ | | | | 120.7 (q) | |
| 8/8″ | | | | 149.3 (q) | |
| 9/9″ | | | | 148.8 (q) | |
| 9a/9a″ | | | | 126.2 (q) | |
| 9b/9b″ | | | | 129.1 (q) | |
| 1′/1‴ | | | | 145.9 (q) | |
| 2′/2‴/6′/6‴ | 7.10 d | 8.0 | 1,9-OMe | 128.2 (t) | 1,4′ |
| 3′/3‴/5′/5‴ | 7.29 t | 8.0 | | 128.2 (t) | 1′ |
| 4′/4‴ | 7.20 t | 8.0 | | 125.9 (t) | 2′/6′, 3′/5′ |
| 4/4′-OMe | 3.86 s | | 5 | 56.2 (p) | 4 |
| 8/8′-OMe | 3.62 s | | | 60.7* (p) | 8 |
| 9/9′-OMe | 3.65 s | | 1, 2′/6′ | 60.6* (p) | 9 |

[a] $^1H$ chemical shift values ($\delta$ ppm from $SiMe_4$) followed by multiplicity and then the coupling constants ($J$ in Hz).

[b] Data are given for half molecule.

[c] HMBC correlations from H to C.

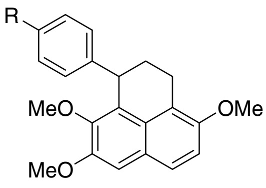
[d] Letters, p, s, t and q, in parentheses indicate, respectively, the primary, secondary, tertiary, and quaternary carbons, assigned by DEPT.

[e] Values with same superscript were exchangeable.

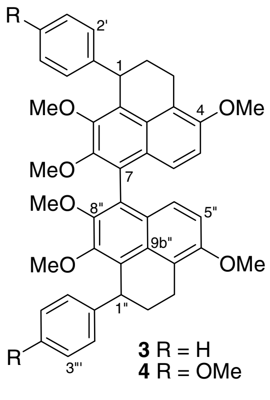
These data indicate a highly symmetric molecule. The carbons were correlated to the respective protons by an HSQC experiment. The analysis of the HMBC data was decisive to revise the structure of the dimeric phenalene **3**. According to the structure in the HMBC spectrum (Table 2) both the H-1/H-1″ and the H-2/H-2″ protons were correlated to the C-3/C-3″ at $\delta$ 18.4 and the C-9a/C-9a″ at $\delta$ 126.2 and C-1′/C-1‴ at $\delta$ 145.9; furthermore, the H-2/H-2″ and H-3/H-3″ protons were correlated to the C-3a/C-3a″ and C-9b/C-9b″ carbons at $\delta$ 120.7 and 129.1, respectively. The H-5/H-5″ and H-6/6″ protons were correlated to the C-4/C-4″ and C-6a/C-6a″ carbons at $\delta$ 152.5 and 125.0, respectively.

The analysis of the NOESY spectrum (Table 2) evidenced NOEs between the H-2′/H-2‴/H-6′/H-6‴ protons with H-1/H-1″, H-2/H-2″ and H-3ax/H-3″ax, the H-5/H-5″ proton with 4/4″-OMe, the H-1/H-1″ and the H-2′/2‴/6′/6‴ protons with 9/9″-OMe. These data confirmed the revised structure of 4,4″,8,8″,9,9″-hexamethoxy-1,1″-diphenyl-2,2″,3,3″-tetrahydro-7,7″-bi(1*H*-phenalene) for compound **3**.

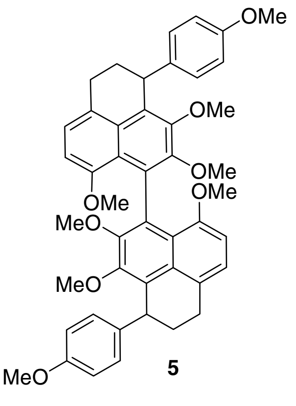
Compound **4** had in the HR-MALDI-MS spectrum a pseudo molecular ion peak at *m*/*z* 727.3189 $[M+H]^+$ and showed 21 carbon signals in the $^{13}C$ NMR spectrum[16] consistent with a molecular formula $C_{46}H_{46}O_8$. The $^1H$ NMR spectrum[16] showed six aromatic protons, four methoxyls, two methylenes and a benzylic methine. These data resembled those of phenalene **3** except for the presence of an additional methoxyl group. Accordingly to the structure, in a NOESY experiment the methoxyl ($\delta$ 3.79) had relation



**1** R = H
**2** R = OMe



**3** R = H
**4** R = OMe



**5**

with the broad doublet at $\delta$ 6.83 assigned to the H-3′/H-3‴/H-5′/H-5‴ protons. Therefore, the revised structure of compound **4** was determined as 4,4″,8,8″,9,9″,4′,4‴-octamethoxy-1,1″-diphenyl-2,2″,3,3″-tetrahydro-7,7″-bi(1*H*-phenalene).

Compound **5** had the same molecular formula as **4** as deduced from a molecular peak at $m/z$ 727.3190 in the HR-MALDI-MS spectrum. The $^{1}$H NMR spectrum (Table 3) showed the presence of one phenyl group with four coupled protons in a AA′XX′ system, two *ortho*-coupled aromatic protons, a benzyl proton, two methylenes, and four methoxyl groups. In the $^{13}$C NMR spectrum (Table 3) 21 carbon signals were present, and the DEPT experiment showed four methyls, two methylenes, five methines, and 10 quaternary carbons. The $^{1}$H and $^{13}$C resonances of dimeric phenalene **5** were assigned by a combination of COSY, NOESY, DEPT, HMQC, and HMBC experiments. The HMBC spectrum of compound **5** showed cross-peaks of H-1 with C-2, C-3, C-9, C-9b, C-1′, and C-2′/C-6′, both the H-2 and the H-3 protons with the C-3a and the C-9b carbons. The C-3a carbon was also correlated to the H-4 and H-5 protons that were both correlated to the C-6 carbon. The analysis of the NOESY spectrum (Table 3) evidenced NOEs between the methoxyl at $\delta$ 3.76 with broad doublet at $\delta$ 3.78 assigned to the H-3′/H-3‴/H-5′/H-5‴ protons; the methoxyl at $\delta$ 3.84 with H-5, and the methoxyl at $\delta$ 3.63 with H-2′/H-2‴/H-6′/H-6‴ and H-1/H-1′ protons. Therefore, the revised structure of compound **5** was determined as 6,6″,8,8″,9,9″,4′,4‴-octamethoxy-1,1″-diphenyl-2,2″,3,3″-tetrahydro-7,7″-bi(1*H*-phenalene).

Table 3
NMR spectral data of compound **5** in $CDCl_3$

| Position | $\delta_H$[a] | $J$ (Hz) | NOESY[b] | $\delta_C$ | HMBC[b,c] |
|---|---|---|---|---|---|
| 1/1″ | 4.94 dd | 4.6, 2.5 | 9-OMe, 2′/6′ | 38.7 (t)[d,e] | 2, 3, 9b, 1′, 2′/6′ |
| 2/2″ | 2.27 | | 2′/6′ | 29.4 (s) | 1, 3, 3a, 9a, 1′ |
| 3ax/3″ax | 2.53 ddd | 16.8, 12.8, 4.8 | 2′/6′ | 18.2 (s) | 1, 2, 3a, 4, 9b |
| 3eq/3″eq | 3.17 ddd | 16.8, 4.8, 2.4 | | | |
| 3a/3a″ | | | | 120.5 (q) | |
| 4/4″ | 7.10 d | 9.0 | | 124.8 (t) | 3, 3a, 6, 9b |
| 5/5″ | 6.99 d | 9.0 | 6-OMe | 111.8 (t) | 3a, 4, 6, 6a |
| 6/6″ | | | | 152.4 (t) | |
| 6a/6a″ | | | | 126.2 (q) | |
| 7/7″ | | | | 113.0 (q) | |
| 8/8″ | | | | 148.8 (q) | |
| 9/9″ | | | | 149.2 (q) | |
| 9a/9a″ | | | | 125.0 (q) | |
| 9b/9b″ | | | | 128.8* (q) | |
| 1′/1‴ | | | | 137.7 (q) | |
| 2′/2‴/6′/6‴ | 6.96 br d | 8.0 | 1, 2, 3ax, 9-OMe | 128.9* (t) | 1, 4′ |
| 3′/3‴/5′/5‴ | 6.78 br d | 8.0 | 4′-OMe | 113.4 (t) | 1′ |
| 4′/4‴ | | | | 157.7 (t) | |
| 6/6′-OMe | 3.84 s | | 5 | 56.0 (p) | 6 |
| 8/8′-OMe | 3.56 s | | | 60.4# (p) | 8 |
| 9/9′-OMe | 3.63 s | | 1, 2′/6′ | 60.8# (p) | 9 |
| 4′/4‴-OMe | 3.76 s | | 3′/5′ | 55.2 (p) | 4′ |

[a] $^{1}$H chemical shift values ($\delta$ ppm from $SiMe_4$) followed by multiplicity and then the coupling constants ($J$ in Hz).

[b] Data are given for half molecule.

[c] HMBC correlations from H to C.

[d] Letters, p, s, t and q, in parentheses indicate, respectively, the primary, secondary, tertiary, and quaternary carbons, assigned by DEPT.

[e] Values with same superscript were exchangeable.

## Acknowledgments

NMR experiments have been performed at Centro Interdipartimentale di Metodologie Chimico-Fisiche of University Federico II of Naples on a 500 MHz spectrometer of Consortium INCA.

## References and notes

1. http://www.invasivespeciesinfo.gov/aquatics/waterhyacinth.shtml#top.
2. (a) DellaGreca, M.; Lanzetta, R.; Molinaro, A.; Monaco, P.; Previtera, L. *Bioorg. Med. Chem. Lett.* **1992**, *2*, 311–314; (b) DellaGreca, M.; Molinaro, A.; Monaco, P.; Previtera, L. *Tetrahedron* **1992**, *48*, 3971–3976.
3. Luis, J. G.; Echeverri, F.; Quinones, W.; Brito, I.; Lopez, M.; Torres, F.; Cardona, G.; Aguiar, Z.; Rojas, M. *J. Org. Chem.* **1993**, *58*, 4306–4308.
4. Luis, J. G.; Fletcher, W. Q.; Echeverri, F.; Grillo, T. A. *Phytochemistry* **1994**, *50*, 10963–10970.
5. Luis, J. G.; Fletcher, W. Q.; Echevarri, F.; Grillo, T. A.; Perales, A.; Gonzalez, J. A. *Tetrahedron* **1995**, *51*, 4117–4130.
6. Luis, J. G.; Quinones, W.; Echeverri, F.; Grillo, T. A.; Kishi, M.; Garcia-Garcia, F.; Torres, F.; Cardona, G. *Phytochemistry* **1996**, *41*, 753–757.
7. Holscher, D.; Schneider, B. *Phytochemistry* **1998**, *49*, 2155–2157.
8. Del Rìo, J. C.; Jimenez-Barbero, J.; Chavez, M. I.; Politi, M.; Gutierrez, A. *J. Agric. Food Chem.* **2006**, *54*, 8744–8748.
9. Cooke, R. G.; Edwards, J. M. *Prog. Chem. Org. Nat. Prod.* **1981**, *40*, 153–190.
10. Holscher, D.; Schneider, B. *Phytochemistry* **1999**, *50*, 155–161.
11. Holscher, D.; Schneider, B. *Phytochemistry* **2005**, *66*, 59–64.
12. Holscher, D.; Reichert, M.; Gorls, H.; Ohlenschlager, O.; Bringmann, G.; Schneider, B. *J. Nat. Prod.* **2006**, *69*, 1614–1617.
13. Holscher, D.; Schneider, B. *J. Nat. Prod.* **2000**, *63*, 1027–1028.
14. (a) Kamo, T.; Hirai, N.; Tsuda, M.; Fujioka, D.; Ohigashi, H. *Biosci. Biotechnol. Biochem.* **2000**, *62*, 95–101; (b) Kamo, T.; Hirai, N.; Iwami, K.; Fujioka, D.; Ohigashi, H. *Tetrahedron* **2001**, *57*, 7649–7656.
15. $^{1}$H NMR: $\delta$ 7.62 (1H, d, $J = 8.8$, H-6), 7.18 (1H, d, $J = 8.8$, H-5), 7.09 (1H, s, H-7), 6.86 (2H, br d, $J = 8.0$, H-2′/H-6′), 6.72 (2H, br d, $J = 8.0$, H-5′/H-3′), 4.84 (1H, dd, $J = 4.4$, 2.4, H-1), 3.95 (3H, s, 4-OMe), 3.91 (3H, s, 8-OMe), 3.73 (3H, s, 4′-OMe), 3.50 (3H, s, 9-OMe), 3.12 (1H, ddd, $J = 16.6$, 4.4, 2.4, H-3eq), 2.49 (1H, ddd, $J = 16.6$, 12.8, 4.4, H-3ax), 2.20 (1H, dddd, $J = 12.8$, 4.4, 2.4, 2.4, H-2eq), 2.09 (1H, dddd, $J = 12.8$, 12.8, 4.4, 4.4, H-2ax). $^{13}$C NMR: $\delta$ 159.1 (C-4′), 151.6 (C-4), 150.8 (C-8), 146.1 (C-9), 137.8 (C-1′), 128.8 (C-2′/C-6′), 128.1 (C-9a), 126.7 (C-9b), 126.2 (C-6a), 125.3 (C-6), 121.2 (C-3a), 113.9 (C-3′/C-5′), 111.9 (C-5), 105.5 (C-7), 60.5 (C-9-OMe), 56.3 (C-4-OMe), 55.4 (C-8-OMe), 55.2 (C-4′-OMe), 38.3 (C-1), 29.1 (C-2), and 18.1 (C-3).

16. $^1$H NMR: (data are given for half molecule): δ 7.07 (1H, d, $J = 8.5$, H-6), 7.04 (1H, d, $J = 8.5$, H-5), 7.00 (2H, br d, $J = 8.5$, H-2′/H-6′), 6.83 (2H, br d, $J = 8.5$, H-5′/H-3′), 4.92 (1H, dd, $J = 4.4$, 2.4, H-1), 3.86 (3H, s, 4-OMe), 3.79 (3H, s, 4′-OMe), 3.64 (6H, s, 8-OMe and 9-OMe), 3.18 (1H, ddd, $J = 16.6$, 4.4, 2.4, H-3eq), 2.53 (1H, ddd, $J = 16.6$, 12.8, 4.4, H-3ax), 2.24 (2H, m, H-2). $^{13}$C NMR: δ 157.7 (C-4′), 152.3 (C-4), 149.1 (C-8), 148.7 (C-9), 137.9 (C-1′), 128.9 (C-2′/C-6′), 128.4 (C-9b), 126.1 (C-9a), 124.5 (C-6a), 124.6 (C-6), 120.6 (C-3a and C-7), 113.5 (C-3′/C-5′), 112.0 (C-5), 60.5 and 60.6 (C-8-OMe and C-9-OMe), 56.0 (C-4-OMe), 55.2 (C-4′-OMe), 37.9 (C-1), 29.7 (C-2), and 18.2 (C-3).