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Dimeric phenylphenalenones from *Musa acuminata* and various Haemodoraceae species. Crystal structure of anigorootin

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Abstract

Three fused octacyclic phenylphenalenone dimers were isolated from *Musa acuminata*: Anigorootin, which was first isolated from *Anigozanthos flavidus* and hitherto represented the only compound of that type, the new 4′-hydroxy-anigorootin, and 4′,4″-dihydroxy-anigorootin, which is a revised structure. The crystal structure of anigorootin was determined by X-ray crystallography. 3,3′-Bis-hydroxyanigorufone, a dimer of the conventional type known from *Anigozanthos preissii*, was also found in *Musa acuminata*. Phytochemical analysis of several Haemodoraceae species revealed the occurrence of anigorootin, 3,3′-bis-hydroxyanigorufone, and the novel metabolite 3,3′-bis-anigorufone. The occurrence of the same compounds in Musaceae and Haemodoraceae indicates the close chemotaxonomic relationship of both plant families. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: *Anigozanthos bicolor*; *Anigozanthos flavidus*; *Anigozanthos preissii*; *Musa acuminata*; *Wachendorfia thyrsiflora*; *Conostylis setosa*; Haemodoraceae; Musaceae; Crystal structure; Dimers; Phenylphenalenones

1. Introduction

Phenylphenalenones represent a class of phenylpropanoid-derived natural products which occur in the Haemodoraceae (Cooke and Edwards, 1980), Pontederiaceae (Greca et al., 1992), Musaceae (genera *Musa* and *Ensete*) (Luis et al., 1993; Hölscher and Schneider, 1998), and Strelitziaceae (Hölscher and Schneider, 2000). Phenylphenalenones from the Musaceae and Haemodoraceae currently are of special interest owing to their potential role as phytoalexins and phytoanticipins (Luis et al., 1993, 1996; Binks et al., 1997; Kamo et al., 2000). A variety of dimeric phenylphenalenones has been isolated from *Eichhornia crassipes* (Pontederiaceae) (Greca et al., 1992), *Anigozanthos* (Haemodoraceae) (Edwards and Hite, 1979; Hölscher and Schneider, 1997, 1999) and *Musa* species (Musaceae) (Luis et al., 1997). In continuation of our research on *Musa* and Haemodoraceae metabolites, we report here the structures of a new fused octacyclic dimeric phenylphenalenone and revision of the structure of a previously reported dimer (Luis et al., 1997), which was found to be of the fused type as well. The X-ray structure of anigorootin, representing the only known compound of this type (Hölscher and Schneider, 1999), is also reported. Additionally, a new conventional dimer was found.

2. Results and discussion

Ethyl acetate extracts from healthy rhizomes of *Musa acuminata* colla AAA var. Cavendish were analyzed by TLC, HPLC, and spectrometric methods for the occurrence of phenylphenalenone type compounds. Six known monomeric phenylphenalenones were identified by means of MS, ^{1}H and ^{13}C NMR data: irenolone (Luis et al., 1993), anigorufone (Cooke and Thomas, 1975), hydroxyanigorufone (Cooke and Thomas, 1975), 2-methoxyanigorufone (Luis et al., 1995b) and *trans*- and *cis*-2,3-dihydro-2,3-dihydroxy-9-phenylphenalen-1-one (Kamo et al., 1998). Two dimeric compounds, anigorootin (**1**) (Hölscher and Schneider, 1999) and 3,3′-

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bis-hydroxyanigorufone (**4**) (Hölscher and Schneider, 1997) were isolated as well, which had previously been isolated from *Anigozanthos flavidus* and *A. preissii*, respectively.

The conventional dimer **4** (Fig. 1) was characterized by NMR and EI–HRMS spectroscopy (*m/z* 574.1423 $[M]^+$, calc. for $C_{38}H_{22}O_6$, 574.1416). NMR data were similar to those of the monomer, hydroxanigorufone, and identical to that of **4** from *A. flavidus*. The NMR data of compound **1** from *Musa acuminata* completely resembled those of anigorootin from *Anigozanthos flavidus* (Hölscher and Schneider, 1999), which demonstrated that the two compounds were identical. The relative configuration of the four stereo centres of anigorootin (**1**) was established from NOE data of the parent compound and acetyl derivatives as all-*R* or all-*S*. These stereochemical data indicated rectangular arrangement of the monomeric units to each other. To study the stereochemistry of this unusual dimer in more detail, X-ray diffraction of a crystal was measured. The centrosymmetrical crystal structure (Fig. 2) indicated a racemic mixture of 7a*R*,7b*R*,14a*R*,14b*R*-**1** and 7a*S*,7b-*S*,14a*S*,14b*S*-**1** in a 1:1 ratio. This racemate crystallized with one molecule of acetone per molecule of the dimer **1**.

In addition to compound **1**, two other dimers of the same structural type were isolated from *Musa acuminata*. In addition to the diagnostic signal of H-7b/H-14b (δ 4.16) three spin systems were detected in the ^1H NMR and ^1H–^1H COSY spectrum of compound **2**. Two corresponded to AB spin systems, attributable to H-2/H-9 (δ 6.98)–H-3/H-10 (δ 7.78) and H-4/H-11 (δ 8.10)- H-5/H-12 (δ 7.41) (Table 1). An AA′BB′ spin system of the exocyclic *p*-substituted phenyl rings was detected by intense doublets of H-2′/2″/6′/6″ (δ 7.31) and H-3′/3″/5′/5″ (δ 6.96), each doublet corresponding to four protons. The singlets at δ 6.85 and δ 8.58 were exchangeable after addition of D_2O, indicating two pairs of equivalent hydroxyl groups in the molecule. Missing signals of further protons indicated substitution at C-1a/C-8a and C-13/C-6 in the molecule. The ^{13}C NMR spectrum of **2** displayed a total of 17 signals, of which two exhibited twice the intensity of the other protonated carbon atoms. These were readily assigned to C-2′/C-2″/C-6′/C-6″ (δ 131.1), C-3′/C-3″/C-5′/C-5″ (δ 115.8). The other protonated carbons C-2/C-9 (δ 119.6), C-3/C-10 (δ 129.8), C-4/C-11 (δ 134.6), C-5/C-12 (δ 129.6), and C-7b/C-14b (δ 33.8) were detected by means of HMQC cross peaks with the corresponding proton signals (Table 1). Mutual HMBC cross signals between H-3/H-10–C-4/C-11 and H-4/H-11–C-3/C-10 were in agreement with the suggested structure of **2**. The signals of oxygenated C-1a/C-8a (δ 152.9) and resonances of the remaining quarternary carbon atoms of the phenylnaphthalene moieties C-7c/C-14c (δ 109.3), C-3a/C-10a (δ 128.8), C-6/C-13 (δ 146.2), C-6a/C-13a (δ 124.4), and C-7d/C-14d (δ 133.9) in addition to the positions of the phenyl rings at C-6 and C-13 were also assigned by HMBC. The HMBC connectivities of the H-7b/H-14b signal established the link between both monomers. Within one monomeric unit, H-7b/H-14b exhibited cross signals *via* three bonds with the carbonyl atoms (C-7/C-14), with C-1a/C-8a, and with the central carbon atoms of the phenalene nuclei C-7d/C-14d. The cross signal between H-7b/H-14b and C-7a/14a (δ 94.3) was due to both a three bond connectivity between both units and a correlation within one unit via two bonds. H-7b/H-14b further correlated with C-7b/C-14b between which signals cross peaks were observed in the HMQC spectrum as well. The signal of the hydroxyl protons (δ 6.85) showed HMBC couplings with C-7/C-14 and C-7b/C-14b. These NMR data, together with ESI–MS (*m/z* 607 $[M+H]^+$) and ESI–HRMS confirmed the suggested structure of compound **2**. This compound has been reported previously as a furane type dimer (compound No. **3** in Luis et al., 1997) and its structure is now revised. On the basis of these measurements another inaccurate structure (compound No. **2** in Luis et al., 1997) is shown to be identical with anigorootin (**1**).

The NMR spectrum of compound **3** (Table 1) displayed signals at the characteristic chemical shift value of H-7b/H-14b (δ 4.17/4.18) of fused phenylphenalenone dimers. However, this signal and further ^1H and ^{13}C resonances appeared in duplicate, indicating a nonsymmetrical dimer. ^1H–^1H COSY revealed four nonequivalent AB spin systems of H-2/H-9 (δ 7.02, δ 6.99), H-3/H-10 (δ 7.82, δ 7.79), H-4/H-11 (δ 8.16, δ 8.11) and H-5/H-12 (δ 7.42, δ 7.40) of the octacyclic nucleus. An

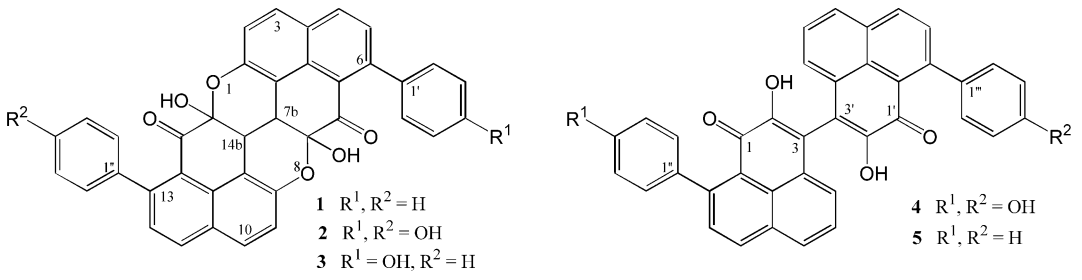

Fig. 1. Structures of dimeric phenylphenalenones from *Musa acuminata* (**1–4**) and various species of the Haemodoraceae family (**1**, **4**, **5**).

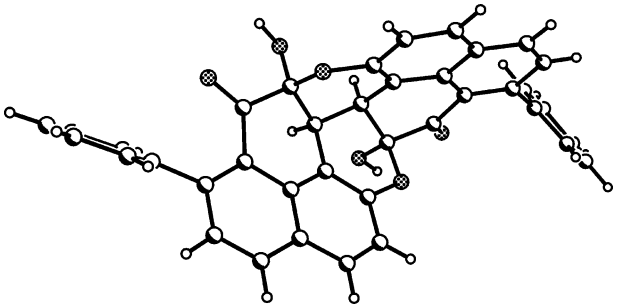

Fig. 2. Molecular structure of compound **1**.

AA′BB′ system showed doublets of H-2′/H-6′ (δ 7.31) and H-3′/H-5′ (δ 6.96) indicative of a para-substituted aromatic ring. A multiplet between δ 7.50 and δ 7.43, corresponding to five protons, showed cross signals only with themselves in the ^{1}H–^{1}H COSY spectrum, typical of a mono-substituted phenyl ring. The singlet at δ 8.57 (1H) was attributable to the phenolic *p*-hydroxyl group and those at δ 6.86/6.85 to OH-7a/OH-14a, as they were exchangeable after addition of D_2O. The HMBC and HMQC connectivities within the octacyclic nucleus and with the exocyclic aryl rings closely resembled those of compounds **1** and **2**. From these data the structure of compound **3** was elucidated as 4′-hydroxyanigorootin, representing a heterodimer in which both parts differ in the substitution of the exocyclic phenylring only. ESI–MS (*m*/*z* 591 $[M+H]^+$) and ESI–HRMS confirmed the suggested dimeric structure of **3**, which is described here for the first time.

Further phytochemical analysis of several Haemodoraceae species by means of NMR and MS techniques revealed the occurrence of dimeric phenylphenalenones as well. Thus, compound **1**, first isolated from *Anigozanthos flavidus* (Hölscher and Schneider, 1999) was detected by means of HPLC–NMR analysis also in root cultures of *A. preissii* and in plants of *Wachendorfia thyrsiflora*. 3,3′-Bis-hydroxyanigorufone (**4**) was identified in extracts of *A. preissii* and *A. bicolor* root cultures. Another new dimer of the conventional C-3,C-3′-linked type was isolated from the *n*-hexane soluble fraction of roots of *A. flavidus* and *Conostylis setosa* plants. ^{1}H and ^{13}C NMR spectra of the new compound **5** closely resembled those of anigorufone. However, the absence of a H-3 signal in the ^{1}H NMR spectrum and the HMBC correlation of H-4/H-4′ (δ 7.72) with a quarternary carbon attributable to C-3/C-3′ indicated a homodimer. Further HMBC and HMQC correlations in addition to EI–MS data (*m*/*z* 542 $[M]^+$) confirmed the structure of this compound as 3,3′-bis-anigorufone (**5**).

From the results described here a close chemotaxonomical relationship between Musacaeae and Haemodoraceae families is evident, since both families of plants not only produce phenylphenalenone-type compounds but, moreover, identical compounds were found in both families. The biosynthesis of phenylphenalenones has been established by feeding experiments using species of either of these families (Thomas, 1971; Harmon and Edwards, 1975; Hölscher and Schneider, 1995a,b; Schmitt and Schneider, 1999; Schmitt et al., 2000;

Table 1
^{1}H and ^{13}C NMR spectral data (500 MHz for ^{1}H; 125 MHz for ^{13}C; acetone-d_6, TMS int. standard) of phenylphenalenone dimers **2**, **3** and **5**

2			**3**		**5**		
Position	δ ^{1}H (*J* in Hz)	δ ^{13}C	δ ^{1}H (*J* in Hz)	δ ^{13}C	Position	δ ^{1}H (*J* in Hz)	δ ^{13}C
1a,8a		152.9		152.9	1,1′		180.1
2,9	6.98 *d* (*J* = 8.9)	119.6	7.02 *d* (*J* = 8.9), 6.99 *d* (*J* = 8.9)	119.54, 119.88	2,2′		148.9
3,10	7.78 *d* (*J* = 8.9)	129.8	7.82 *d* (*J* = 8.9), 7.79 *d* (*J* = 8.9)	129.88, 129.90	3,3′		118.2
3a,10a		128.8		129.15, 129.18	3a,3′a		129.5
4,11	8.10 *d* (*J* = 8.4)	134.6	8.16 *d* (*J* = 8.4), 8.11 *d* (*J* = 8.4)	134.65, 134.80	4,4′	7.72 *d* (*J* = 7.2)	130.4
5,12	7.41 *d* (*J* = 8.4)	129.6	7.42 *d* (*J* = 8.4), 7.40 *d* (*J* = 8.4)	129.6	5,5′	7.59 *dd* (*J* = 7.2, 8.2)	128.0
6,13		146.2		146.0, 146.2	6,6′	8.12 *d* (*J* = 8.2)	130.7
6a,13a		124.4		124.4	6a,6′a	–	132.9
7,14		191.2		191.3	7,7′	8.48 *d* (*J* = 8.2)	136.6
7a,14a		94.3		94.27, 94.31	8,8′	7.69 *d* (*J* = 8.2)	132.0
7b,14b	4.16 *s*	33.8	4.17 *d* (*J* = 5.6), 4.18 *d* (*J* = 5.6)	33.76, 33.78	9,9′		149.5
7c,14c		109.3		109.29, 109.42	9a,9′a		124.7
7d,14d		133.9		133.9	9b,9′b		126.2
1′,1″		133.5		133.5	1″,1‴		143.8
2′,6′	7.31 *d* (*J* = 8.6)	131.1	7.31 *d* (*J* = 8.5)	131.1	2″,6″		129.1
3′,5′	6.96 *d* (*J* = 8.6)	115.8	6.96 *d* (*J* = 8.5)	115.8	3″,5″	7.43–7.49 *m*	128.9
4′		158.1		158.1	4″		128.1
2″,6″	7.31 *d* (*J* = 8.6)	131.1		128.1	2‴,6‴		129.1
3″,5″	6.96 *d* (*J* = 8.6)	115.8	7.43–7.50 *m*	129.6	3‴,5‴	7.43–7.49 *m*	128.9
4″		158.1		128.8	4‴		128.1
7a-OH,14a-OH	6.85 *s*		6.86 *s*, 6.85 *s*				
4′-OH	8.58 *s*		8.57 *s*				
4″-OH	8.58 *s*						

Kamo et al., 2000). However, there are no studies focussing specifically on the formation of phenylphenalenone dimers. The dimers described here are linked through a C-3/C-3′ bond, the position which is adjacent to the hydroxyl group at C-2 of the monomers. Thus, phenol oxidative coupling is likely to be involved in this dimerization. Anigorufone and hydroxyanigorufone clearly are precursors of 3,3′-bis-anigorufone (**4**) and 3,3′-bis-hydroxyanigorufone (**5**), respectively. Whether or not these C-3/C-3′-dimers are intermediates in the route leading to the fused dimers remains unclear. It is more plausible that 4-hydroxyanigorufone, a phenylphenalenone recently isolated from *Anigozanthos flavidus* (Hölscher and Schneider, 1999), is the precursor of the fused dimers. Due to strong sterical hindrance of a hypothetical 2,2′,4,4′-tetrahydroxylated intermediate, atropic isomers might exist, which easily twice undergo intramolecular addition at the $\Delta_{2,3}$ double bonds in an *anti* fashion resulting in the fused dimer, anigorootin (**1**). During that process, the first intramolecular addition fixes the conformation in such a way that the formation of the second semi acetal bond is stereospecifically controlled. However, since there are two hypothetical atropic isomers from which the first intramolecular addition can start, both the 7a*R*,7b*R*,14a*R*,14b*R*- and 7a*S*,7b*S*,14a*S*,14b*S*-isomers are formed. The formation of a more thermodynamically stable compound may be the driving force for this kind of cyclization.

3. Experimental

3.1. Plant material

Healthy rhizomes of *Musa acuminata* (colla AAA) cv. 'Cavendish' were supplied by Instituto Colombiano Agropecuario (ICA), Colombia. Plants of Haemodoraceae species were obtained from the botanical gardens of the Universities of Halle/S. (Germany) (*Anigozanthos flavidus*), Berlin-Dahlem (*Conostylis setosa*), and Düsseldorf (*Wachendorfia thyrsiflora*). Root cultures of *Anigozanthos preissii* and *Anigozanthos bicolor* were established as previously described (Hölscher and Schneider, 1997).

3.2. Extraction and purification

Freshly collected rhizomes of *Musa acuminata* (20 kg) were washed, chopped, pressed to eliminate water, and immediately extracted with ethanol (2 l) in a percolator system. The crude extracts were evaporated to 25% of the initial volume and the residue was extracted with EtOAc (Luis et al., 1995a,b). Compounds **1–4** were purified by preparative TLC using Et_2O/*n*-hexane (7:1 v/v) as eluent. Further purification was achieved by means of reversed-phase HPLC (UV 254 nm) on a LiChrosphere 100 RP-18 column (250×4 mm), 5 μm; a linear gradient MeCN containing 0.1% triflouroacetic acid (TFA) – H_2O (0.1% TFA) from 30 to 70% MeCN in 35 min at a flow rate of 1 ml min^{-1} was used. Compound **1** (from *Musa acuminata*, 1.0 mg) was crystallized from acetone using a Dewar for slow solvent evaporation. Amounts isolated from *Musa acuminata* were as follows **2**: 1.4 mg, **3**: 0.8 mg, **4**: 2.1 mg. Roots of *Anigozanthos flavidus* plants (450 g fresh mass) were extracted with methanol, evaporated, and the residue was partitioned between *n*-hexane and H_2O. The organic phase was evaporated and separated by reversed-phase HPLC using the conditions described above to obtain compound **5** (1.1 mg). Using the same procedure, compound **5** (0.7 mg) was also obtained from roots of *Conostylis setosa* (90 g fresh mass). Compound **4** (2.1 mg) was isolated from root cultures of *Anigozanthos bicolor* (100 g fresh mass) as described previously from *A. preissii* (Hölscher and Schneider, 1997). Anigorootin (**1**) was also detected in extracts of root cultures of *A. preissii* and roots of *Wachendorfia thyrsiflora* plants by means of HPLC-NMR analysis following published protocols (Hölscher and Schneider, 1997) without isolation.

3.3. Spectroscopic methods

^1H and ^{13}C NMR, ^1H–^1H COSY, HMBC, and HMQC spectra were recorded on Bruker AMX 300 and Bruker Avance DRX 500 NMR spectrometers. With the Avance DRX 500, an inverse detection microprobe head (2.5 mm) was used at 500.13 MHz for acquisition of ^1H NMR, ^1H–^1H COSY, and heteronuclear 2D correlation spectra, and a broadband decoupled microprobe head (2.5 mm) for measuring ^{13}C NMR spectra at 125.75 MHz. Acetone-d_6 was used as a solvent and TMS as internal standard. EI–MS were run on a Micromass MasSpec mass spectrometer at 70 eV. ESI–MS and ESI–HRMS were measured in the positive ion mode on a Micromass Quattro II tandem quadrupole mass spectrometer.

3.4. X-ray diffraction

The intensity data for the compound **1** were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated MoK_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption (Otwinowski and Minor, 1997). The COLLECT data collection software, Nonius B.V., Netherlands, 1998 was used. The structure was solved by direct methods (SHELXS) (Sheldrick, 1990) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97) (Sheldrick, 1997). The hydrogen atoms were located by difference Fourier synthesis and refined isotropically. The nonhydrogen atoms were refined anisotropically (Sheldrick, 1997). XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

3.5. 7b,14b-Dihydro-7a,14a-dihydroxy-6,13-diphenyl-(7H,14H)-diphenalen[2,3,3a,4-b,c,d:2,3,3a,4-g,h,i]pyrano[4,3-c]pyran-7,14-dione (anigorootin, **1**)

NMR and MS spectra are identical with published data (Hölscher and Schneider, 1999). Crystal data: $C_{38}H_{22}O_6$ * C_3H_6O, Mr = 632.63 g mol^{-1}, colourless prism, size 0.08×0.08×0.06 mm^3, triclinic, space group P-1, a = 9.3054(3), b = 10.9797(5), c = 15.7591(7) Å, α = 107.542(2), β = 99.495(2), γ = 95.317(2)°, V = 1496.8(1) Å^3, T = −90 °C, Z = 2, $\rho_{calc.}$ = 1.404 g cm^{-3}, μ (Mo K_α) = 0.96 cm^{-1}, $F(000)$ = 660, 10767 reflections in $h(-11/12)$, $k(-14/14)$, $1(-19/20)$, measured in the range $2.39° \leqslant \Theta \leqslant 27.48°$, completeness Θ_{max} = 98.7%, 6776 independent reflections, R_{int} = 0.052, 4245 reflections with $F_o > 4\sigma(F_o)$, 545 parameters, 0 restraints, $R1_{obs}$ = 0.047, wR^2_{obs} = 0.109, $R1_{all}$ = 0.083, wR^2_{all} = 0.122, GOOF = 0.934, largest difference peak and hole: 0.200/−0.213 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-173674. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44)1223–336–033; e-mail: deposit@ccdc.cam.ac.uk).

3.6. 7b,14b-Dihydro-7a,14a-dihydroxy-6,13-di-(4-hydroxyphenyl)-(7H,14H)-diphenalen[2,3,3a,4-b,c,d:2,3,3a,4-g,h,i]pyrano[4,3-c]pyran-7,14-dione (4′,4″-dihydroxy-anigorootin, **2**)

Pale yellow solid. ESI–MS: m/z (rel. int.) 607 $[M+1]^+$ (100). ESI–HRMS: m/z 607.1409 (calc. 607.1393 for $C_{38}H_{23}O_8$). ^{1}H and ^{13}C NMR, see Table 1.

3.7. 7b,14b-Dihydro-7a,14a-dihydroxy-6-(4-hydroxyphenyl)-13-phenyl-(7H,14H)-diphenalen[2,3,3a,4-b,c,d:2,3,3a,4-g,h,i]pyrano[4,3-c]pyran-7,14-dione (4′-hydroxy-anigorootin, **3**)

Pale yellow solid. ESI — MS: m/z (rel. int.) 591 $[M+1]^+$ (100). ESI — HRMS: m/z 591.1446 (calc. 591.1444 for $C_{38}H_{23}O_7$). ^{1}H and ^{13}C NMR, see Table 1.

3.8. 3,3′-Bis-anigorufone (**5**)

Orange solid. EIMS (70 eV): m/z (rel. int.) 542 (58), 271 (100). ^{1}H and ^{13}C NMR, see Table 1.

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