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Three dimeric anthracene derivatives from the fruits of *Bulbine abyssinica*

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Dedicated to Professor Wolfgang Steglich on the occasion of his 70th birthday

Abstract—From the fruits of *Bulbine abyssinica* three new dimeric anthracene derivatives, (*P*)-8,9,1′,8′-tetrahydroxy-3,3′-dimethyl[10,7′-bianthracene]-1,4,9′,10′-tetraone (trivial name abyquinone A), (10*R*)-1,4,8,1′,8′-pentahydroxy-3,3′-dimethyl-[10,7′-bianthracene]-9,9′,10′(10*H*)-trione (trivial name abyquinone B), and (10*R*)-3′,4′-dihydro-1,4,8,3′,8′,9′-hexahydroxy-3,3′-dimethyl-[10,7′-bianthracene]-9,1′(10*H*,2′*H*)-dione (trivial name abyquinone C) were isolated. Despite their structural differences, these three compounds are connected to each other by the apparently biomimetic conversion of abyquinone C (a preanthraquinonylanthrone with two stereogenic centers) into B (an anthraquinonylanthrone with one stereogenic center) and finally into A (an axially chiral bianthraquinone) under mild conditions, involving a highly efficient center-to-axis chirality transfer. In addition, the known anthraquinones islandicin and chrysophanol were identified. The structures were determined on the basis of spectroscopical evidences, chemical transformations, and quantum chemical CD calculations.

1. Introduction

The genus *Bulbine* (Asphodelaceae) comprises about 40 species,[1] of which *B. abyssinica* and *B. frutescens* are the only ones found in Kenya. While the former is an indigenous species,[2] the latter is widely cultivated for aesthetic purposes.[3] In traditional medicine, *Bulbine* species are used for the treatment of various ailments including infections.[4] In South Africa, *B. asphodeloides* is taken as a styptic, for scrofula, dehydration, and for palpitation,[5] while *B. latifolia* is used to treat rheumatism, diarrhea, and dysentery.[6]

The presence of anthraquinones, including phenylanthraquinones, and isofuranonaphthoquinones in *Bulbine* species has been reported,[3,6–10] and from the roots of *B. abyssinica*, also some anthraquinones have been isolated.[7,9] In this paper, we describe the isolation and characterization of three dimeric anthracene derivatives (**1**, **2**, and **3**), along with two known anthraquinones from the fruits of *B. abyssinica*.

2. Results and discussion

Compound **1** was isolated as a dark-red amorphous powder. The UV (λ_{max} 232, 256, 303, 438, 471, 500, 542 and 582 nm) suggested an anthraquinone chromophore. The presence of four chelated hydroxy protons (δ 17.04, 12.30, 11.95 and 10.51 in the ^{1}H NMR spectrum, see Table 1), four carbonyl resonances (δ 193.4, 186.8, 184.3 and 182.2 in the ^{13}C NMR spectrum), two methyl groups (at δ 2.03 and 2.50 in ^{1}H NMR, 17.3 and 22.5 in ^{13}C NMR), and the molecular ion peak in the EIMS (*m*/*z* 506) showed this compound to be a dimeric anthraquinone derivative.[11,12]

From the NMR (Table 1) spectra, one half of the molecule was established to be a 9,10-anthraquinone derivative, viz a chrysophanol moiety, exhibiting two broad ^{1}H NMR singlets at δ 7.14 and 7.72, assigned to H-2′ and H-4′, respectively, and with a methyl group (δ 2.50) located at

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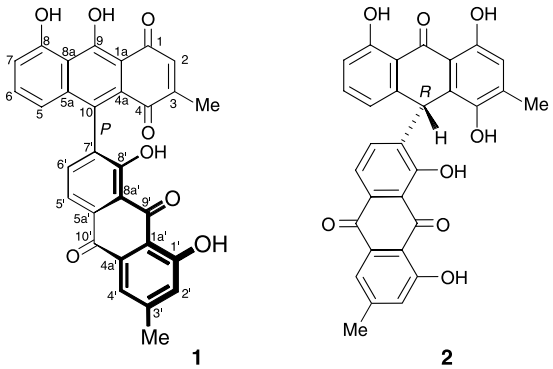
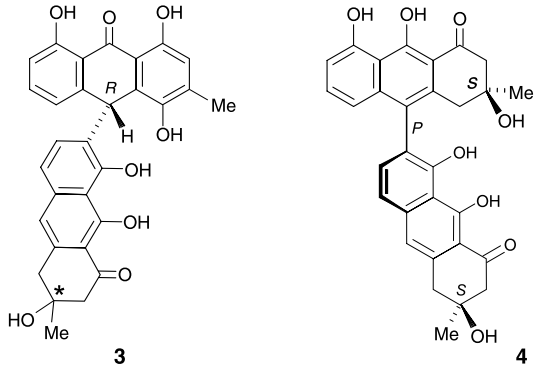




C-3′. Two *ortho*-coupled ($J=8.0$ Hz) protons at δ 7.95 and 7.43 were attributed to H-5′ and H-6′, respectively, with C-7′ of the chrysophanol moiety being substituted.

For the other half of the molecule, the ^{1}H NMR signals at δ 17.04 and 10.51 (for two chelated hydroxy protons) and the ^{13}C NMR signals at δ 182.2 and 186.8 for two carbonyl groups) suggested the presence of a 1,4-anthraquinone skeleton.[11,12] The long-wavelength UV absorption maxima (λ_{max} 500, 542 and 582 nm) in compound **1** were in agreement with the presence of such a moiety.[11,12] In the 1,4-anthraquinone part an AMX spin system at δ 6.93 (dd, $J=1.5$, 8.0 Hz), 7.51 (t, $J=8.0$ Hz), and 7.10 (dd, $J=1.5$, 8.0 Hz) was assigned to H-5, H-6 and H-7, respectively. A one-proton quartet ($J=1.2$ Hz) was assigned to H-2, which showed a long-range coupling with Me-3 (δ 2.03, d, $J=$ 1.2 Hz). This assignment was confirmed by a NOESY correlation between H-2 and Me-3. This left C-10 of the 8,9-dihydroxy-3-methyl-1,4-anthraquinone moiety to be the point of attachment to the chrysophanol moiety, thus suggesting a 10,7′-linkage in compound **1**. This connection was confirmed by an HMBC correlation of H-6′ with C-10 and a NOESY interaction between H-5 and H-6′. From these data the new natural product was characterized as 8,9,1′,8′-tetrahydroxy-3,3′-dimethyl[10,7′-bianthracene]-1,4,9′,10′-tetraone, for which the trivial name abyquinone A (**1**) was suggested. The compound was optically active indicating the presence of a non-racemic axially chiral biaryl. In the CD spectrum of **1**, a positive Cotton effect at 276 nm and a negative one at 301 nm, that is, nearly opposite to those reported for the *P*-configured dimeric preanthraquinone peroxisomicine A_1 (**4**),[13] indicated abyquinone A (**1**) to have the opposite stereoarray at the chiral axis, so that, due to the formalism of the CIP denotation, a *P*-configured axis was expected for **1**, too.

In order to determine the absolute configuration at the chiral axis in a reliable, non-empirical way, quantum chemical CD calculations were performed.[14,15] Arbitrarily starting with the *P*-atropo-enantiomer of abyquinone A (**1**), the molecule was submitted to a conformational analysis using the semiempirical AM1[16] method, resulting in eight optimized minimum geometries within the energetically relevant range of 3 kcal/mol above the global minimum. For each single geometry thus obtained, a CD spectrum was calculated using the semiempirical CNDO/S[17] as well as the OM2[18] Hamiltonian. In both cases the individual spectra were then added and weighted following the Boltzmann statistics, that is, according to the respective heats of formation. The two overall CD spectra thus obtained, were subsequently UV corrected[19] and compared with the experimental CD curve of **1**. Both when following the CNDO/S approach (Fig. 1(a)) and the OM2 method (Fig. 1(b)), a good agreement between the measured spectrum and those predicted for (*P*)-**1** was obtained (Fig. 1, left), whereas the CD curves computed for (*M*)-**1** were virtually opposite as compared to the experimental one (Fig. 1, right). Consequently, the chiral axis of **1** was clearly assigned to be *P*-configured.

The second compound (**2**) was isolated as an amorphous yellow powder. The EIMS ($[M]^+$ at *m/z* 508, $C_{30}H_{20}O_8$), as well as ^{1}H and ^{13}C NMR (Table 1) spectra suggested a bianthracene skeleton. Comparison of the ^{1}H and ^{13}C NMR spectra of **2** with those of **1** (Table 1) showed that one half of the molecule was again a chrysophanol moiety coupled to the second half of the molecule via C-7′.

For that other moiety, the ^{1}H NMR (Table 1) displayed signals for two chelated hydroxy groups (δ 11.95 and 12.35 for OH-1 and OH-8), aromatic protons with an AMX spin system (δ 6.95, dd, $J=1.5$, 8.0 Hz for H-5; 7.41, t, $J=$ 8.0 Hz for H-6; 6.88, dd, $J=1.5$, 8.0 Hz for H-7), an up-field shifted aromatic methyl group (δ 2.26 for CH_3-3), a broad singlet for an aromatic proton (δ 6.79 for H-2), and a methine proton (6.20, s, for H-10) suggesting that this moiety was 1,4,8-trihydroxy-3-methylanthrone, which was connected to the other half of the compound via C-10. The ^{13}C NMR was in agreement with the presence of a carbonyl function (δ 193.1), three hydroxy groups (δ 157.6, 144.5, and 162.9 for C-1, -4, and -8, respectively), and a methine unit (δ 35.8 for C-10) in this half of the molecule. The 10,7′-linkage in this compound was confirmed by HMBC correlations of H-10 with C-6′, -7′, and -8′, and by NOESY interactions of H-10 with H-6′ and OH-8′, thus suggesting **2** to be 1,4,8,1′,8′-pentahydroxy-3,3′-dimethyl-[10,7′-bianthracene]-9,9′,10′(10*H*)-trione, which was henceforth given the trivial name abyquinone B.

The configurational assignment of abyquinone B (**2**) was again achieved by means of the AM1-Boltzmann approach as described above for compound **1**. In this case, the conformational analysis resulted in two conformers within the range of 3 kcal/mol above the global minimum, and the overall CD spectra received with the OM2[18] approach on the SCI (Fig. 2(a)) and the SDCI (Fig. 2(b)) levels led to the unambiguous attribution of the chiral center of **2** to be *R*-configured (Fig. 2, right).

Table 1. ^{1}H and ^{13}C NMR data δ together with HMBC (^{2}J and ^{3}J) correlations of **1**, **2**, and **3**

	1			**2**			**3**		
	^{1}H	^{13}C	HMBC	^{1}H	^{13}C	HMBC	^{1}H	^{13}C	HMBC
1		182.2			157.6			157.5	
1a		108.3			113.2			113.0	
2	6.97 q	134.8	4, 9a	6.79 br s	118.5	1a, 4, 3-Me	6.72 br s	118.2	3, 3-Me
3		152.5			137.4			138.1	
4		186.8			144.5			145.2	
4a		134.0			127.0			127.1	
5	6.93 dd	120.6	6, 8a, 10	6.95 dd	120.0	8a	6.87 dd	120.5	7, 10
5a		138.1			144.4			145.9	
6	7.51 t	134.4	5a, 8	7.41 t	137.1	5a, 8	7.38 t	137.0	5a, 8
7	7.10 dd	116.7	5, 8, 8a	6.88 dd	116.5	5	6.84 dd	116.1	5, 8
8		160.1			162.9			162.9	
8a		116.2			115.5			115.7	
9		170.1			193.1			194.0	
10		132.3		6.20 s	35.8	1a, 4, 4a, 5, 5a, 8a, 6′, 7′, 8′	6.13 s	35.0	1a, 4, 4a, 5, 5a, 8a, 6′, 7′, 8′
1′		163.2			163.0			204.4	
1a′		114.3			113.8			110.7	
2′	7.14 br s	124.7	1a′, 4′	7.12 br s	124.6	4′	2.86 br s	51.6	1a′, 1′
3′		150.2			150.8			71.4	
4′	7.72 br s	121.7	1a′, 2′, 10′	7.60 br s	121.8	1a′, 2′, 4a	3.06 br s	43.5	1a′, 10′
4a′		134.9			133.5			136.5	
5′	7.95 d	120.3	7′, 8a′, 10′	7.59 d	120.5	7′	6.98 d	120.5	7′, 10′
5a′		133.5			132.5			138.7	
6′	7.43 d	137.3	5a′, 8′, 10	7.18 d	136.8	10a′	6.84 d	132.0	5a′, 8′
7′		136.3			138.4			123.6	
8′		160.9			158.4			152.1	
8a′		115.8			116.8			112.9	
9′		193.4			194.2			164.8	
10′		184.3			181.5		6.93 s	118.1	1a′, 4′, 5′, 5a′, 8a′
Me-3	2.03 d	17.3	2, 3, 4	2.26 s	17.5	2, 3, 4	2.18 s	17.5	2
Me-3′	2.50 s	22.5	2′, 3′, 4′	2.55 s	22.4	2′, 3′, 4′	1.4 s	29.4	
OH-1				11.95 s		1, 1a	11.96 s		1, 1a, 2
OH-8	10.51 s			12.35 s		8, 8a	12.36 s		7, 8
OH-9	17.04 s		1a						
OH-1′	11.95 s		1′, 2′	11.87 s		1′, 1a′, 2′			
OH-8′	12.30 s		7′, 8′, 8a′	13.16 s			10.74 s		
OH-9′							16.12 s		

$J_{5,6}=J_{6,7}=J_{5',6'}=8.0$ Hz; $J_{5,7}=1.5$ Hz; in **1** $J_{2,Me\text{-}3}=1.2$ Hz.

Compound **3** was isolated as a yellowish brown amorphous powder. The NMR spectra (Table 1) of this compound, as for **2**, once again suggested the presence of a bianthracene derivative in which one half is a 1,4,8-trihydroxy-3-methylanthrone moiety coupled via C-10. The comparison of the NMR spectra of **3** with those of prechrysophanol (**5**)[20] indicated the substituent at C-10 to be such an anthracenone moiety. The only difference observed was that the AMX system in **5** was now replaced by two *ortho*-coupled doublets at δ 6.98 and 6.84 ($J=8.0$ Hz), which suggested either C-5′ or C-7′ in the preanthraquinone moiety of **3** to be substituted. The latter—and thus a 10,7′-linkage in compound **3**—was confirmed by an HMBC correlation of H-10 with C-6′, -7′, and -8′, and also by NOESY correlations of H-10 with H-6′ and OH-8′. EIMS showed a weak molecular ion peak at *m/z* 512, with a fragment ion at *m/z* 494 as a result of the loss of one molecule of water, which was in agreement with **3** being a bianthracene derivative containing a prechrysophanol moiety. The fragment ions at *m/z* 254 and 240 corresponded to the monomeric portions of **3**, that is, resulting from a cleavage of the 10,7′-linkage, with subsequent loss of water. By these investigations, the constitution of **3** was identified as 3′,4′-dihydro-1,4,8,3′,8′,9′-hexahydroxy-3,3′-dimethyl-[10,7′-bianthracene]-9,1′(10*H*,2′*H*)-dione, for which the trivial name abyquinone C was suggested.

The CD spectrum of abyquinone C (**3**) exhibited Cotton effects very similar to those obtained for abyquinone B (**2**) at 230, 270, and 300 nm. Hence the absolute configuration at C-10, as the chiral center dominating the CD behavior of **3**, should also be *R*, whereas a reliable conclusion about the absolute stereostructure at C-3′, which has a much lower influence on the molecular CD, was not possible at that stage.

For the determination of the absolute configurations of **3** at its two stereogenic centers, C-10 and C-3′, again quantum chemical CD calculations were performed. Since not even the relative configuration of these two chiral centers was known, two independent conformational analyses, for the (10*S*,3′*R*)- and the (10*S*,3′*S*)-diastereomer of **3**, were launched, resulting in both cases in 28 minimum structures within the range of 3 kcal/mol above the global minimum. While both overall simulated CD spectra for (10*S*,3′*R*)-**3** and (10*S*,3′*S*)-**3** behaved virtually oppositely compared with

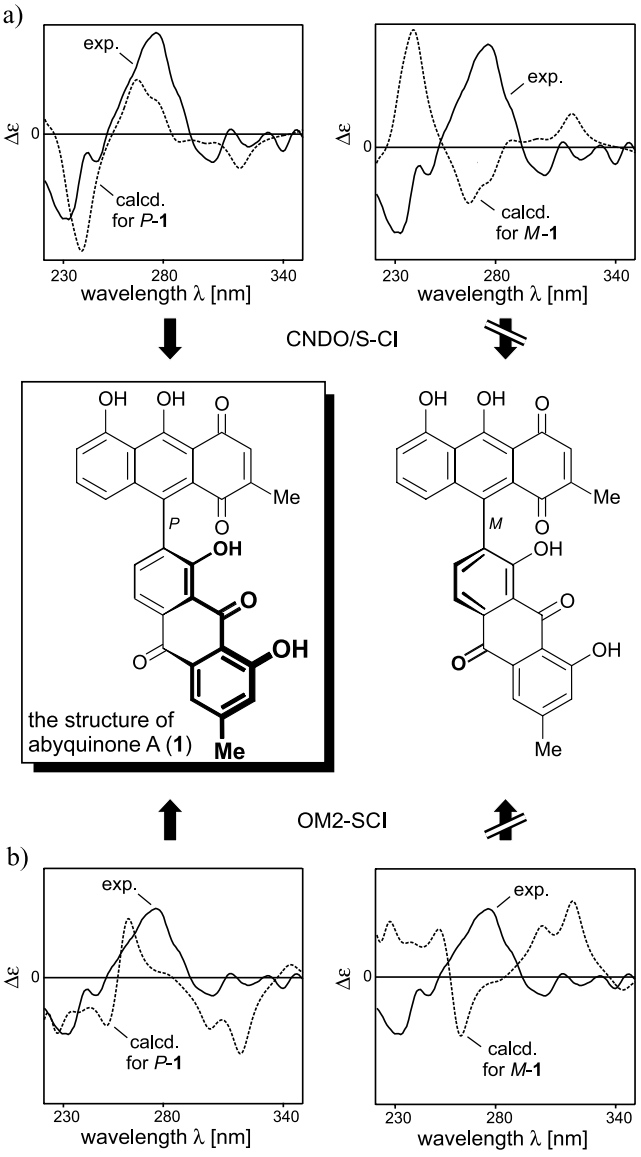
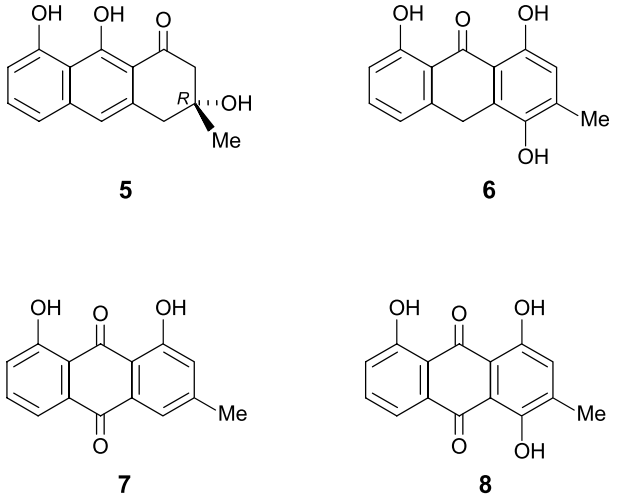


Figure 1. Attribution of the absolute configuration of abyquinone A (**1**) by comparison of the experimental CD spectrum with the spectra calculated for (*P*)-**1** and (*M*)-**1**; (a) using the CNDO/S and (b) the OM2 Hamiltonian.

the experimental curve (Fig. 3, left), a good agreement for the measured CD spectrum with both spectra computed for (10*R*,3′*S*)-**3** and (10*R*,3′*R*)-**3** was obtained (Fig. 3, right), thus, at least, assigning the stereocenter at C-10 to be *R*-configured. This result was in accordance with the above determined *R*-configuration of **2** and the easy transformation of **3** into **2** by dehydration and oxidation (see below).

A closer look at the two calculated CD spectra matching the measured one (Fig. 3, right) suggests that the absolute configuration at C-3′ of abyquinone C (**3**) should be *S*, due to the slightly better agreement of the computed curve for (10*R*,3′*S*)-**3** in the short wavelength area with the experimental one. This, however, can only be regarded as a tendency and remains to be confirmed by chemical or biochemical methods, like by total synthesis,[21] by biosynthetic investigations,[22] or by degradation,[13] which is presently in progress.[23]

Compound **3** appears to originate from the oxidative coupling of the precursors prechrysophanol[24] (**5**) and islandicin anthrone (**6**). In accordance with this assumption, chrysophanol (**7**) and islandicin (**8**) themselves were also isolated and identified along with the new compounds **1**–**3** from the fruits of *B. abyssinica*.



Upon aerial oxidation under basic conditions, compound **3** was converted into **2** and subsequently into **1**. This suggested that compound **3** is the biosynthetic precursor to **1** in the plant, too, whereas **2** is an intermediate. All of the three compounds, **1**, **2**, and **3** were also detected (by TLC) in the crude ethyl acetate extract, clearly indicating that these substances are genuine natural products and not artefacts.

Besides the smooth course of these presumably biomimetic reactions, the stereochemical implications are of particular interest. While the dehydration of **3** to give **2** simply implies the loss of one stereogenic center, with the remaining one being expectedly the same in **3** and **2**, as confirmed by the quantum chemical CD calculations, the formation of **1** from **2** involves the loss of the only stereogenic center and the new formation of a rotationally hindered biaryl axis. This reaction occurs with a remarkable center-to-axis chirality transfer. The direction of the asymmetric induction—(*R*)-**2**→(*P*)-**1**—can be explained in terms of the global minimum structure of **2** shown in Fig. 4 (left), in which the 'Southern' molecular portion is firmly locked in an array with the 'trioxy front' directed above the plane, fixed by a strong hydrogen bond of the proton of OH-4 with the oxygen of OH-8′. This pre-orientation is apparently fully retained during the oxidative conversion of **2** to abyquinone A (**1**), thus leading to a *P*-configuration at the originating chiral axis (Fig. 4, right).

The conversion is likely to be highly efficient in terms of chirality transfer, since the precursors **3** and **2**, as well as the final product **1**, were obtained in enantiomerically pure forms as evidenced by their chromatographic analysis on a chiral phase and by examination of their CD spectra. This chirality transfer, so far undescribed in natural products chemistry, merits further attention for synthetic purposes.[25]

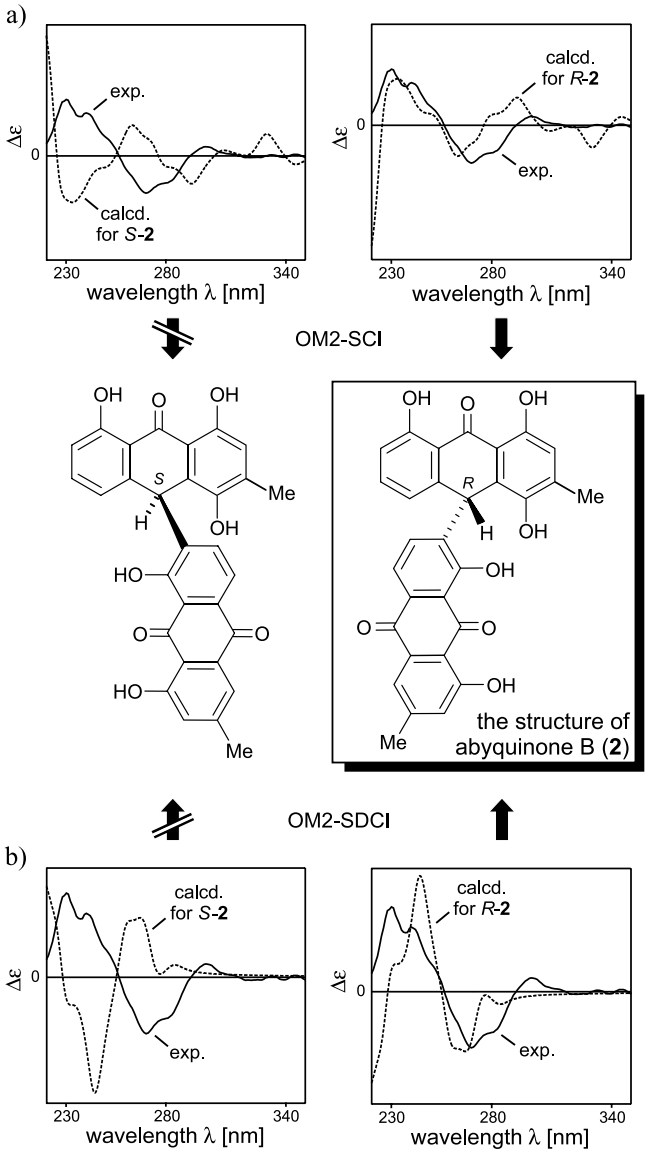


Figure 2. Assignment of the absolute configuration of abyquinone B (**2**) by comparison of the experimental CD spectrum with the spectra calculated for (*S*)-**2** and (*R*)-**2** using the OM2 Hamiltonian (a) with an SCI and (b) using an SDCI calculation.

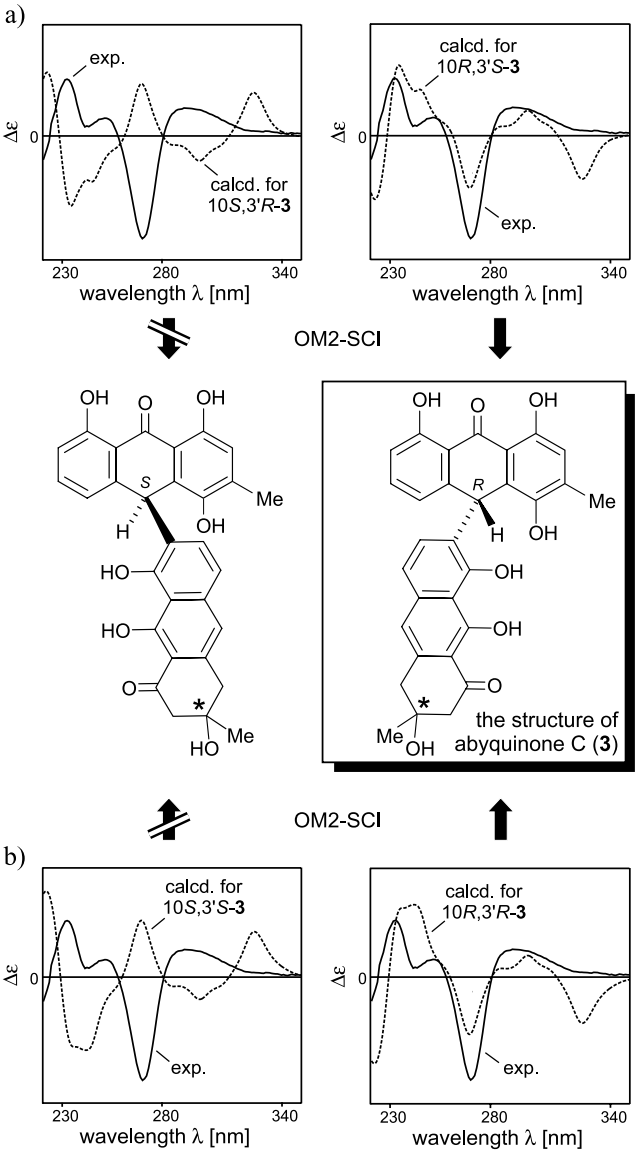


Figure 3. Attribution of the absolute configuration of abyquinone C (**3**) by comparison of the experimental CD spectrum with the spectra calculated for (a) (10*S*,3′*R*)-**3** and (10*R*,3′*S*)-**3** and (b) (10*S*,3′*S*)-**3** and (10*R*,3′*R*)-**3** using in both cases the OM2 Hamiltonian with an SCI calculation.

3. Conclusion

The work described in this paper presents the isolation and structural assignment of a series of three new dimeric anthracene derivatives, abyquinones A, B, and C, by using a combined approach of spectroscopic methodes, chemical transformations, and quantum chemical CD calculations. Accordingly, **2** and **3** have an identical configuration at C-10 (both *R*), whilst in the case of **3** the absolute configuration at C-3′ could not be elucidated with certainty, although the computations suggest the stereogenic center to be *S*-configured. The absolute configuration of the rotationally hindered biaryl axis of **1** was unambiguously assigned as *P*. The results demonstrate the value of combining experimental and computational methods in attaining configurational information and explaining stereochemical behavior otherwise difficult to achieve. Certainly of biosynthetic

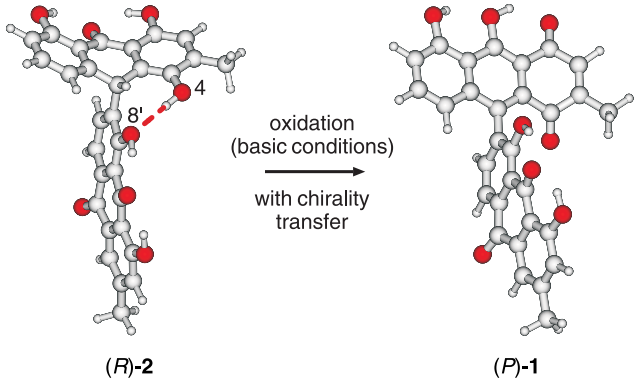


Figure 4. Center-to-axis chirality transfer from abyquinone B (**2**) to abyquinone A (**1**). The *R*-configuration in **2** induces a *P*-configured chiral axis in **1** due to the pre-orientation initiated by the hydrogen bond between OH-4 and OH-8′; both structures shown constitute global AM1 minimum geometries.

relevance, the preanthraquinonylanthrone **3**, upon standing under basic conditions in the presence of air, gives the anthraquinonylanthrone **2**, which is further converted to the axially chiral bianthraquinone **1**, apparently without loss of enantiomeric purity, hinting at a center-to-axis chirality transfer as yet unprecedented for natural products, in particular under so mild conditions.

4. Experimental

4.1. General

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. IR spectra were taken on a Jasco FT/IR-410 spectrometer. UV spectra were recorded on a Varian Cary 50 probe spectrophotometer. Analytical TLC: Merck pre-coated silica gel 60 F_{254} plates. CC on oxalic acid impregnated silica gel 60 (70–230 mesh). EIMS: direct inlet, 70 eV on a SSQ 710, Finnigan MAT spectrometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) on Bruker spectrometer using TMS as int. standard. HMQC and HMBC spectra were acquired using the standard Bruker software. CD spectra were recorded on a Jasco J-715 spectropolarimeter and optical rotations on a Jasco P-1020 polarimeter (using a sodium D line and a quartz cuvette with 1 cm path length and 1 cm i.d.).

4.2. Plant material

Fruits of *Bulbine abyssinica* were collected near Thika town along the Nairobi-Thika highway in August 1994. The plant was identified at the University Herbarium, Department of Chemistry, University of Nairobi, where a voucher specimen (SGM-AYT-1994-06) has been deposited.

4.3. Extraction and isolation

The dried and ground powder (150 g) of the fruits of *Bulbine abyssinica* was extracted with ethyl acetate by cold percolation. The crude extract (3.5 g) was chromatographed on oxalic acid impregnated silica gel (100 g), eluting with increasing polarities of mixtures of *n*-hexane/dichloromethane and then ethyl acetate/dichloromethane. A total of 23 fractions, each ca. 200 ml, were collected and combined into seven major fractions (A to G).

The methanol soluble portion of fraction C (eluted with 20% dichloromethane in *n*-hexane) was crystallized from dichloromethane/*n*-hexane to give islandicin (3 mg) as red crystals (R_f 0.5 on 5% ethyl acetate in *n*-hexane). PTLC (5% ethyl acetate in *n*-hexane) separation of fraction D (eluted with 30% dichloromethane in *n*-hexane), gave further amounts of islandicin (4 mg) and chrysophanol (16 mg) as a yellow crystalline compound (R_f 0.4 on 5% ethyl acetate in *n*-hexane). Fraction E (eluted with 40% dichloromethane in *n*-hexane) was crystallized from dichloromethane/ *n*-hexane to give compound **1** (55 mg) as a dark red amorphous powder (R_f 0.7, dichloromethane). Fraction F (eluted with 50% dichloromethane in *n*-hexane) showed two spots on TLC (10% ethyl acetate in dichloromethane). PTLC separation (oxalic acid impregnated silica gel, solvent dichloromethane) and subsequent crystallization from dichloromethane/*n*-hexane yielded compound **2** (43 mg) as a yellowish brown powder. Fraction G (eluted with 5% ethyl acetate in dichloromethane) was purified by CC on Sephadex LH 20 (CH_2Cl_2–MeOH; 1:1) to give compound **3** (15 mg).

4.3.1. Abyquinone A (1). Dark red amorphous powder; mp 161 °C (CH_2Cl_2); $\alpha_D^{20} = -248°$ (*c* 0.02, CH_2Cl_2, mean value; the measured α_D values varied from −200 to −300 due to the long-wavelength UV absorbance;[26–28] IR (NaCl): 3452, 1667, 1618, 1427, 1381, 1269, 1132, 1073, 1025, 1004, 965, 885, 754 cm^{-1}; UV/Vis (MeOH): λ_{max} (log ε) = 232 (3.83), 256 (3.60), 303 (3.00), 438 (3.26), 471 (3.20), 500 (3.01), 542 (3.02), 582 (2.60) nm; CD (CH_2Cl_2): $\Delta\varepsilon_{229}$ −12.4, $\Delta\varepsilon_{276}$ 10.5, $\Delta\varepsilon_{301}$ −2.5; ^{1}H NMR (Table 1); ^{13}C NMR (Table 1); EIMS *m/z* (rel. int.): 506 (M^+, 100), 489 (61), 281 (23); HREIMS *m/z* 506.0993 (M^+; calcd for $C_{30}H_{18}O_8$, 506.1002).

4.3.2. Abyquinone B (2). Yellowish brown amorphous powder; mp 184 °C (MeOH); $\alpha_D^{20} = -25.2°$ (*c* 0.02, MeOH); IR (NaCl): 3431, 1662, 1621, 1420, 1379, 1259, 1122, 1069, 1025, 885, 754 cm^{-1}; UV/Vis (MeOH): λ_{max} (log ε) = 232 (3.92), 256 (3.60), 303 (3.00), 438 (3.18), 467 (2.78) nm; CD (CH_2Cl_2): $\Delta\varepsilon_{230}$ 10.1, $\Delta\varepsilon_{237}$ 7.0, $\Delta\varepsilon_{240}$ 7.7, $\Delta\varepsilon_{270}$ −6.7, $\Delta\varepsilon_{300}$ 1.6; ^{1}H NMR (Table 1); ^{13}C NMR (Table 1); EIMS *m/z* (rel. int.): 508 (M^+, 20), 489 (8), 281 (24), 254 (25); HREIMS *m/z* 508.1153 (M^+; calcd for $C_{30}H_{20}O_8$, 508.1158).

4.3.3. Abyquinone C (3). Yellow amorphous powder; mp 193 °C (MeOH); $\alpha_D^{20} = -63.5°$ (*c* 0.1, MeOH); IR (NaCl): 3428, 1633, 1620, 1600, 1485, 1284, 1124, 775 cm^{-1}; UV/Vis (MeOH): λ_{max} (log ε) = 232 (4.09), 276 (3.91), 398 (3.48) nm; CD (MeOH): $\Delta\varepsilon_{194}$ 2.8, $\Delta\varepsilon_{208}$ −2.4, $\Delta\varepsilon_{212}$ −1.5, $\Delta\varepsilon_{218}$ −2.6, $\Delta\varepsilon_{230}$ 1.8, $\Delta\varepsilon_{241}$ −0.1, $\Delta\varepsilon_{251}$ 1.2, $\Delta\varepsilon_{273}$ −4.8, $\Delta\varepsilon_{323}$ 1.1; ^{1}H NMR (Table 1); ^{13}C NMR (Table 1); EIMS *m/z* (rel. int.): 512 (M^+, 3), 494 (6), 493, (7), 474 (16), 254 (100), 240 (67); HREIMS *m/z* 512.1465 (M^+; calcd for $C_{30}H_{24}O_8$, 512.1471).

4.4. Aerial oxidation

Compound **3** (10 mg) was dissolved in 5% methanolic KOH and the mixture was stirred for 2 h at room temperature. The solution was acidified and extracted with dichloromethane. Preparative TLC purification of the organic layer gave compound **1** (trace), **2** (5 mg) and unreacted **3** (3 mg). In a separate experiment compound **3** (5 mg) was completely converted to **1** (3 mg) when the methanolic solution was stirred for 3 d. Compound **2** was also converted to **1** in a similar experiment. The reactions were monitored by TLC and the identity of the products was confirmed by ^{1}H NMR analysis.

4.5. Computational

The conformational analyses were performed on a Linux AMD MP 2400+ workstation by means of the semi-empirical AM1[16] method as implemented in the program

package Gaussian 98,[29] starting from preoptimized geometries generated by the TRIPOS[30] force field as part of the molecular modeling package SYBYL 6.9.[30] The wave functions required for the computation of the rotational strengths for the electronic transitions from the ground state to excited states were obtained by CNDO/S[17] calculations followed by SCI computations including 625 singly occupied configurations and the ground state determinant, and by OM2[18] calculations followed by SCI and SDCI calculations including 900 singly and 400 doubly occupied configurations, respectively, and the ground state determinant. These computations were also carried out with a Linux AMD MP 2400+ workstation using the BDZDO/MCDSPD[31] program package, and by the use of the MNDO99[32] software package. The single CD spectra were summed up and weighted following the Boltzmann statistics, that is, according to the respective heats of formation. The rotational strengths were transformed into $\Delta\varepsilon$ values and for a better visualization superimposed with a Gaussian band shape function.

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