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Austrocolorins A_1 and B_1: atropisomeric 10,10′-linked dihydroanthracenones from an Australian *Dermocybe* sp.[1]

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Dedicated to Prof. Dr. Wolfgang Steglich on the occasion of his 70th birthday

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Abstract

The atropisomeric austrocolorins A_1 (**7**) and B_1 (**8**), new members of the rare tricolorin class of 10,10′-coupled dihydroanthracenones, are isolated from an indigenous Australian toadstool belonging to the subgenus *Dermocybe* of *Cortinarius*, and their structure and absolute central and axial configuration is deduced from the spectroscopic data, and confirmed by chemical degradation and chiral HPLC analysis.

Keywords: *Dermocybe* sp. WAT 26641; Cortinariaceae; Pigments; Dihydroanthracenone dimers; Atropisomers; Austrocolorins

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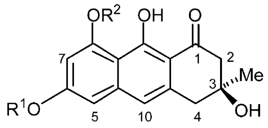
1. Introduction

Oxidative coupled dimers of dihydroanthracenone such as atrochrysone (**1**), torosachrysone (**2**) and the 8-*O*-methyl ether **3** of torosachrysone (**2**) enjoy a widespread distribution in toadstools belonging to the genus *Cortinarius* and its allies (Gill and Steglich, 1987; Gill, 1994, 1996, 1999). Whereas the 7,7′-coupled dimers (referred to as the flavomannins) are the most widespread group, the 5,5′- and 7,10′-dimers (the atrovirins and phlegmacins, respectively) and the 5,10′-dimers (psuedophlegmacins) are less common, being found among only a few species (Gill and Steglich, 1987; Oertel, 1984; Steglich and Oertel, 1984). In contrast, there are only two recorded examples of fungal dimers in which the dihydroanthracenone moieties are linked between C 10 and C 10′. Thus, tricolorin A (**4**) and its acetate derivative **5** were first detected in extracts of the fruit bodies of *Leucopaxillus tricolor* (Besl and Bresinski, 1977) and subsequently isolated and characterised as the unique 10,10′-coupled dimers **4** and **5**



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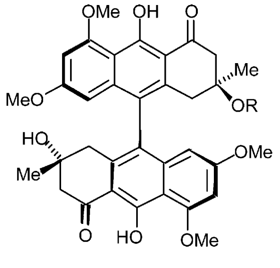
3 $R^1 = R^2 = Me$



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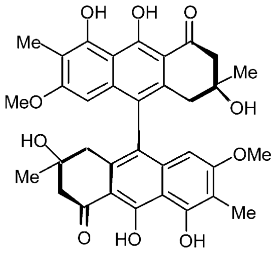
5 R = Ac



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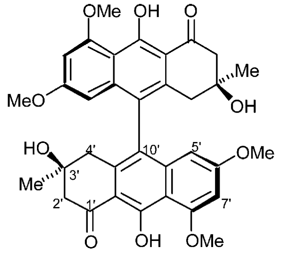

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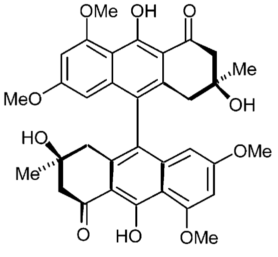

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[1] Part 71 in the series Pigments of fungi; for Part 70 see Cotterill et al. (2003).

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Table 1
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) for the pigments **7**, **8** and torosachrysone 8-*O*-methyl ether (**3**)

Proton	Chemical shift (δ), multiplicity and coupling constant (*J* Hz)		
	Austrocolorin A_1 (**7**)	Austrocolorin B_1 (**8**)	(**3**)
H_{eq} 2,2′	2.79 (2H, br *s*)	2.85 (br *d*, 18.5)	2.84
H_{ax} 2,2′		2.80 (*d*, 18.5)	2.82
3,3′-Me	1.22 (*s*)	1.26 (*s*)	1.42
H_{eq} 4,4′	2.41 (*dd*, 16.6 and 2.0)	2.48 (br *d*, 16.4)	3.06 (2H, *d*, 16.4)
H_{ax} 4,4′	2.77 (*d*, 16.6)	2.58 (*d*, 16.4)	
H 5,5′	6.03 (*d*, 2.5)	6.05 (*d*, 2.3)	6.56 (*d*, 2.2)
H 7,7′	6.47 (*d*, 2.5)	6.47 (*d*, 2.3)	6.43 (*d*, 2.2)
H 10,10′	–	–	6.84 (br *s*)
6,6′-OMe	3.51 (*s*)	3.49 (*s*)	3.91 (*s*)
8,8′-OMe	4.03 (*s*)	4.03 (*s*)	3.98 (*s*)
9,9′-OH	15.45 (*s*)	15.48 (*s*)	15.08 (*s*)

(Besl et al., unpublished; Gill and Steglich, 1987). The (*M*)-absolute configuration at the biaryl axis in both **4** and **5** followed from the sign of the Cotton effect in the CD spectrum (Harada and Nakanishi, 1983; Eliel and Wilen, 1994) and by spectroscopic comparison with singueanol 1 (**6**), a bioactive constituent of the medicinal plant *Cassia singueana* (Endo and Naoki, 1980). Interestingly, most signals in the ^{1}H NMR spectrum of **4** are doubled, an observation best rationalized by the presence in **4** of two stereogenic centres of *opposite* absolute configuration. The alternative rationale, that tricolorin A (**1**) might exist as a mixture of diastereoisomers cannot be dismissed but it is rendered less likely by the fact that the ^{1}H NMR spectrum of the mono-acetate **5** shows only a single set of signals in accord with the structure **5** shown.

We describe here the isolation of two new, atropisomeric 10,10′-coupled dihydroanthracenone dimers, **7** and **8**, the first members of this rare group of natural products to be isolated from a fungus belonging to the genus *Cortinarius*.

The structure and absolute central and axial configuration of each of these pigments, which we have called the austrocolorins A_1 (**7**) and B_1 (**8**), are deduced from the respective ^{1}H NMR and CD spectra and confirmed by reductive cleavage of **4** and subsequent chiral HPLC analysis of the fragments.

2. Results and discussion

The fruit bodies of the rare *Dermocybe* sp. WAT 26641[2] are typically small (4–7 cm in height) even at maturity, but are spectacularly colourful. The cap skin has deep purple striations, the gills are mustard yellow and the stipe is bright yellow with vivid purple ring zones. The base of the stem and the subterranean mycelium are a bright yellow colour and, consequently, the mycelium can be distinguished and collected with minimum contamination with soil debris. We first collected the fruit bodies and mycelium *D.* sp. WAT 26641 in the Kinglake National Park, Victoria, during June 1994 and again from the same location during several subsequent seasons. Preliminary TLC analysis of the organic solvent-soluble extractives of the fruit bodies and the mycelium of *D.* sp. WAT 26641 revealed that both extracts have essentially the same pigment profile and, consequently, we will not differentiate between them herein.

After maceration and filtration, the EtOH extracts of fresh collections of *D.* sp. WAT 26641 were evaporated to dryness and the residue was partitioned between EtOAc and water. TLC of the EtOAc phase shows the presence of two mobile bright yellow zones and two, less mobile, pale yellow bands that are strongly fluorescent when viewed under UV light (λ_{max} 365 nm). The chemical composition of the more mobile, bright yellow zones will be discussed in detail elsewhere. The structure and stereochemistry of the two fluorescent, more polar pigments are addressed here.

The fluorescent yellow bands (R_F 0.19 and 0.25) present in the TLC of *D.* sp. WAT 26641 were separated by a combination of PTLC and gel permeation through Sephadex LH-20. The more abundant pigment, austrocolorin A_1 (**7**) (no stereochemical detail yet intended) was obtained as optically active, yellow prisms (from toluene-petrol), m.p. 146–147 °C, in 1.9×10^{-2}% yield). The mass spectrum of **7** shows an abundant molecular ion at *m*/*z* 602, from which the molecular formula $C_{34}H_{34}O_{11}$ followed from the high resolution mass measurement. The molecular formula, together with the IR (ν_{max} 3415 and 1605 cm^{-1}) and UV–vis. (λ_{max} 231, 271, 316 and 394 nm) data of **7** are suggestive of a dimer of the coupled torosachrysone type (Gill and Steglich, 1987). This suggestion is supported by the ^{1}H and ^{13}C NMR data for **7**, which are collected, juxtaposed with

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[2] The code refers to the accession number under which lyophilised voucher specimens are held in the herbarium of the Royal Botanic Garden, Edinburgh, UK.

the corresponding data for torosachrysone 8-*O*-methyl ether (**3**), in Tables 1 and 2, respectively. It follows from analysis of the ^1H NMR spectra of **7** and **3** that both contain (i) a signal from a strongly chelating phenolic hydroxy group, (ii) two *meta* coupled aromatic proton doublets, (iii) signals from two aromatic *O*-methyl groups, and (iv) a couplet characteristic of a 3-hydroxy-3-methyldihydroanthracenone system. The presence in the ^1H NMR spectrum of **7** of signals from less than half the number of hydrogen atoms in the molecular formula (the C 3 and C 3′ hydroxy protons are not observed) implies that austrocolorin A_1 is composed of two identical halves. Furthermore, the absence from the spectrum of **7** of a signal that could be assigned to H 10 and H 10′ suggests that the site of the biaryl coupling in **7** is between C 10 in one half and C 10′ in the other. The C 10–C 10′ biaryl linkage in **7** is corroborated by the up-field shift of the signals assigned to 3,3′-Me, H_2 4,4′, H 5,5′ and 6,6′-OMe, when compared to their counterparts in **3** due to anisotropic shielding by the adjacent naphthalene ring (Gill and Steglich, 1987).

The same structural arguments can be made for the less abundant fluorescent pigment, austrocolorin B_1 (**8**) (no stereochemistry yet implied), isolated after chromatography as an optically active, yellow-green powder, m.p. 139–141 °C, in a yield of 2×10^{-3}% of the fresh weight of the fungus. The mass spectrum of **8** contains an abundant molecular ion at m/z 602 and high resolution mass measurement leads to the formula $C_{34}H_{34}O_{11}$, confirming the isomeric relationship between the austrocolorins A_1 (**7**) and B_1 (**8**). The IR (ν_{max} 3443 and 1606 cm^{-1}) and the UV–vis. spectrum (λ_{max} 231, 272, 318, and 395 nm) of **8** are very similar to the corresponding data for **7** and the close relationship is further reflected in the ^1H and ^{13}C NMR data (Tables 1 and 2). Table 2 also contains the results of direct and long-range ^1H–^{13}C heteronuclear correlation experiments, which are fully supportive of the (gross) formulae **7** and **8**.

In total, the spectroscopic data shows clearly that the austrocolorins A_1 (**7**) and B_1 (**8**) are diastereoisomers, but they do not, as yet, differentiate between whether **7** and **8** share the same stereogenicity at C 3 and C 3′ or, instead, are atropisomers.

The CD spectra of atropisomerically enriched coupled biaryls, including pre-anthraquinones such as **7** and **8**, are characterized by a strong bisignate Cotton effect couplet centred near 275 nm due to ‘exciton coupling’ between the asymmetrically disposed aromatic chromophores (Harada and Nakanishi, 1983; Eliel and Wilan, 1994). Consequently, the shape of the CD spectra of coupled binaphthyls such as **7** and **8** correlates directly to the axial configuration (Gill and Steglich, 1987; Oertel, 1984). Accordingly, a binaphthyl in which the two chromophores are related by an anticlockwise helical twist exhibit a negative Cotton effect at longer wavelength and a positive one at shorter wavelength (a so-called ‘A-type’ curve). The alternative (one in which the chromophores describe a clockwise twist) gives rise to a CD spectrum in which the signs of the Cotton effects are inverted (known as a ‘B-type’ curve) (Gill and Steglich, 1987; Oertel, 1984). The CD spectra of the pigments **7** and **8** are shown in Fig. 1, from which it is evident that these natural products are atropisomeric. Furthermore, the spectrum of austrocolorin A_1 (**7**) represents an ‘A-type’ curve consistent with ‘negative chirality.’ In the case of **7** this corresponds to the *M* axial configuration according to the Prelog–Helmchen rules (Prelog and Helmchen, 1982). Conversely, the CD spectrum of austrocolorin B_1 (**8**) shows a ‘B-type’ curve (‘positive chirality’) and therefore, *P* axial chirality in **8**.

Table 2
^{13}C NMR data ($CDCl_3$, 100 MHz) and short- and long-range heteronuclear correlations for austrocolorins A_1 (**7**) and B_1 (**8**)

Carbon	Chemical shift (δ_C)	Correlated protons		
	7	**8**	HMQC	HMBC
1,1′	202.2	202.2	–	H_{eq} 2,2′, H_{ax} 2,2′
2,2′	50.8	51.3	H_{ax} 2,2′, H_{eq} 2, 2′	H_{eq} 4,4′, H_{ax} 4,4′, 3,3′-Me
3,3′	71.1	70.4	H 3,3′	H_{eq} 4,4′, H_{ax} 4,4′, 3,3′-Me
3,3′-Me	30.2	29.4	3,3′-Me	–
4,4′	39.8	41.5	H_{ax} 4,4′, H_{eq} 4,4′	H_{eq} 2,2′, 3,3′-Me
4a,4a′	136.3	136.1	–	H_{eq} 4,4′, H_{ax} 4,4′
5,5′	97.8	97.4	H 5,5′	–
6,6′	162.4	162.7	–	H 7,7′, 6,6′-OMe
6,6′-OMe	55.2	55.2	6,6′-OMe	–
7,7′	98.0	98.2	H 7,7′	H 5,5′
8,8′	161.8	161.8	–	8,8′-OMe
8,8′-OMe	56.3	56.3	8,8′-OMe	–
8a,8a′	110.6	110.7	–	H 5,5′, H 7,7′, 9-OH
9,9′	165.7	165.8	–	9-OH
9a,9a′	110.0	109.7	–	9-OH
10,10′	124.0	123.6	–	H_{eq} 4,4′, H_{ax} 4,4′, H 5,5′
10a,10a′,	141.6	141.3	–	–

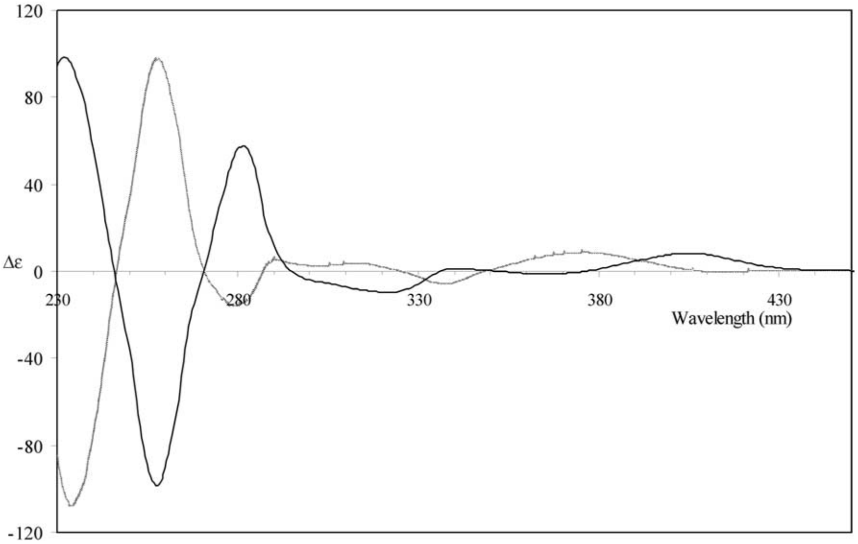

Fig. 1. Circular dichroism spectra of the austrocolorins A_1 (**7**) (—) and B_1 (**8**) (—) (EtOH).

Since the austrocolorins A_1 (**7**) and B_1 (**8**) are atropisomers but not enantiomers, they must have the same absolute configuration at the C 3 and C 3′ chiral centres. To determine the absolute configuration we first examined the ^{1}H NMR chemical shifts and coupling constants for both H_{eq} 4,4′ and H_{ax} 4,4′ in **7** and in **8** (Table 1). In recent years there has evolved a reliable, empirical correlation between the difference ($\Delta\delta$) between (i) the chemical shift of H_{eq} 4,4′ and H_{ax} 4,4′, (ii) the configuration at the biaryl axis and (iii) the chirality of the C 3 and C 3′ centres in molecules of this type that are connected either at C 5 or C 10 (Gill, 1999; Oertel, 1984). This has so far been applied and validated by chemical methods with pigments of the atrovirin (Morgan, 1998; Gill and Morgan, 2004), phlegmacin (Elsworth et al., 1999) and psuedophlegmacin (Buchanan et al., 1999) types. It is not applicable in the 7,7′-linked (flavomannin) series but chemical methods have been developed in this case (Gill et al., 1990).

In effect, in those dimers in which the C 3 hydroxy group (which occupies an axial configuration in molecules of this type) is on the *same* face of the dihydroanthracenone to which it is connected as the bulk of the C 10 (or C 5) appended dihydroanthracenone moiety then there is a relatively large chemical shift difference ($\Delta\delta = 0.15$–0.25 ppm) between H_{eq} 4,4′ and H_{ax} 4,4′. On the other hand, when the C 3 hydroxy group and the C 10 (or C 5) appendage are on opposite sides of the molecule then the chemical shift difference is much smaller ($\Delta\delta \leqslant 0.08$ ppm). This phenomenon and its application in this area was first developed and applied by Oertel (1984) who was party to the introduced the terms ′syn′ and ‘anti’ to describe these two relative orientations (Steglich and Oertel, 1984). Consequently, once the CD spectrum is recorded, inspection of the ^{1}H NMR spectrum of a binaphthyl of this type allows deduction of the central stereochemistry. In the case of austrocolorin A_1 (**7**), a large $\Delta\delta$ between H_{eq} 4,4′ and H_{ax} 4,4′ (0.36 ppm) indicates a ‘syn’ arrangement and, therefore, the absolute configuration at C 3 and C 3′ in (**7**) must be (*S*). Similarly, the corresponding data for austrocolorin B_1 (**8**) shows a $\Delta\delta$ of 0.1 ppm, which is consistent only with an ‘anti’ relationship and, therefore, the (*S*) absolute configuration at C 3 and C 3′ in (**8**).

The absolute configuration at the stereogenic centres in **7** (and therefore the validity of the method) was confirmed chemically by brief exposure of **7** to alkaline sodium dithionite in order to effect reductive cleavage of the biaryl bond. The reaction mixture so obtained was purified by gel permeation to afford (*S*)-torosachrysone 8-*O*-methyl ether (**3**), which proved identical (^{1}H NMR, CD) with an authentic sample (Gill et al., 1990). The (*S*) stereochemistry of the degradation product **3** was determined by comparison of the HPLC retention time over a chiral phase of **3** obtained from **7** with that of the major enantiomer in an anisochiral sample of **3** in which the (*S*)-enantiomer is known to predominate (72% e.e.). The chromatogram showed no trace of **ent-3** and shows that **7** occurs naturally in at least 98% e.e.

Disappointingly, despite the nicely crystalline nature of austrocolorin A_1 (**7**), numerous attempts to obtain crystals suitable for X-ray crystallographic analysis have failed.

3. Conclusions

The austrocolorins A_1 (**7**) and B_1 (**8**), new examples of rare 10,10′-coupled dihydroanthracenone dimers of the tricolorin class are isolated for the first time from a fungus belonging to the ubiquitous genus *Cortinarius*. The axial and the central stereochemistry of **7** and **8** are determined unambiguously by spectroscopic and chemical methods that also serve to confirm earlier speculation regarding the absolute configuration of tricolorin A (**4**) and its naturally occurring acetate derivative **5** (Gill and Steglich, 1987; Oertel, 1984). This paper is the first report of the unequivocal determination of the absolute central chirality of a fungal 10,10′-linked dihydroanthracenone dimer.

4. Experimental

4.1. General

Melting points were determined on a hot-stage apparatus and are uncorr. IR spectra were recorded using a Perkin-Elmer 983 G spectrophotometer for samples as KBr discs. Electronic spectra were recorded on a Varian SuperScan 3 spectrophotometer in EtOH in a 10 mm quartz cell. NMR spectra were recorded with JEOL JNM-GX-400 and Varian Unity 400 spectrometers (^{1}H at 400 MHz and ^{13}C at 100 MHz) for solutions in $CDCl_3$. Mass spectra were recorded on V. G. Micromass 7070F and JEOL JMS AX505H spectrometers at 70 eV (probe). Specific rotations were measured in $CHCl_3$ using a Perkin-Elmer 241MC polarimeter and are given in units of 10^{-1} deg^2 cg^{-1}. CD spectra were acquired using an AVIV 62DS spectrometer for solutions in MeOH.

4.2. Materials

TLC and PTLC were performed on Merck pre-coated silica gel 60 F_{254} and Merck Kieselgel 60 GF_{254} (20 g silica gel spread on 20×20 cm glass plates), respectively. Visualisation took place under UV light (254 or 366 nm). R_F-values were measured using toluene–HCO_2Et–HCO_2H (50:49:1) as eluent. Subsequent gel permeation (GPC) employed a column (40×3.5 cm) of Sephadex LH-20 suspended in and eluted with MeOH.

Dermocybe sp. WAT 26641 was collected from the Kinglake National Park, Victoria, Australia from mixed *Eucalyptus* and *Leptospermum* forest during May and June 1994 and again in several subsequent seasons. It was either used fresh or was stored at −20 °C until needed. Voucher specimens are lodged in the herbarium of the Royal Botanic Garden, Edinburgh, under accession number WAT 26641 and were identified as belonging to *Dermocybe* by Dr. R. Watling, MBE (Edinburgh).

4.3. Extraction and isolation

Fruit bodies (122 g) of WAT 26641 were macerated in EtOH (800 cm^3) at room temperature for 4 h. The yellow-brown extract was evaporated to dryness and the brown residue was partitioned between water (100 cm^3) and EtOAc (3×100 cm^3). The combined organic phases were dried (Na_2SO_4) and evaporated to afford an orange-brown residue (2.3 g) that was purified by PLC using toluene–HCO_2Et–HCO_2H (50:49:1) as eluent. This gave two yellow zones (R_F 0.14 and 0.17) and two, more polar, fluorescent green zones (R_F 0.19 and 0.25). The two fluorescent zones were further purified by gel permeation through a column of Sephadex LH-20 using MeOH as eluent to give the compounds **7** (23 mg, 1.9×10^{-2}% fr. wt.) and **8** (2.5 mg, 2.0×10^{-3}% fr. wt.).

4.3.1. Austrocolorin A_1 (7)

Green prisms, m.p. 146–147 °C (toluene–petrol) (Found: M^+ 602.2138. $C_{34}H_{34}O_{10}$ requires: M 602.2152); $[\alpha]_{D}+288$ (c 0.05, $CHCl_3$); CD 234 ($\Delta\epsilon$, −107.5), 258 (+97.6), 280 (−15.8), 290 (+5.7), 303 (+2.8), 313 (+4.0), 337 (−5.6), 377 (+8.9), 413 nm (−0.2); ν_{max} 3415, 1605, cm^{-1}; λ_{max} 231 (log ϵ 3.28), 271 (3.52), 316(sh), 394 nm (2.93); mass spec. (EI) m/z 602 (M^+, 37%), 584 (20), 148 (21), 85 (100), 83 (99), 69 (27), 59 (21), 57 (29); δ Table 1; δ_C Table 2.

4.3.2. Austrocolorin B_1 (8)

A yellow-green powder, m.p. 139–141 °C (from MeOH) (Found: M^+ 602.2161. $C_{34}H_{34}O_{10}$ requires: M 602.2152); $[\alpha]_D$ −316 (c 0.045, $CHCl_3$); CD 232 ($\Delta\epsilon$, +98.6), 258 (−98.5), 282 (+57.6), 322 (−9.9), 340 (+1.2), 366 (−1.1), 406 nm (+8.2); ν_{max} 3443, 2930, 1606 cm^{-1}; λ_{max} 231 (log ϵ 4.79), 272 (5.10), 318 (4.28), 329(sh) (4.19), 395 nm (4.56); mass spec. (EI) m/z 602 (M^+, 37%), 584 (20), 148 (21), 85 (100), 83 (99), 69 (27), 59 (21), 57 (29); δ Table 1; δ_C Table 2.

4.3.3. Reductive cleavage of austrocolorin A_1 (7)

To a solution of austrocolorin A_1 (**7**) (8 mg) in aqueous NaOH (2 M, 2 cm^3) was added sodium dithionite (50 mg). After 1 min a second portion (50 mg) of sodium dithionite was added and, after a further 3 min, the solution was cooled with ice, neutralized with dilute HCl (10% w/v, ca 1.5 ml), and the products were extracted into EtOAc (2×40 cm^3). The combined organic extract was dried (Na_2SO_4) and evaporated and the residue was applied to a column of Sephadex LH-20 (40×2 cm). Elution of the column with MeOH–CH_2Cl_2 (1:1) gave (*S*)-torosachrysone 8-*O*-methyl ether (**3**) identical by ^{1}H NMR and CD spectroscopy with an authentic sample (Gill et al., 1990).

4.3.4. Chiral HPLC analysis of 3

The sample of **3** obtained as described above was analysed by chiral HPLC [Daicel Chiralpak AD (10 µm; 0.46×25 cm)] by using EtOH as eluent (0.5 cm^3 min^{-1}). (*S*)-Torosachrysone 8-*O*-methyl ether (**3**) was eluted after a retention time of 10.1 min. Under identical conditions an authentic sample of (*S*)-torosachrysone 8-*O*-methyl ether (**3**) of 72% e.e. gave a chromatogram with peaks with retention times of 10.1 (major) and 28.7 min (minor). There was no material eluting after a retention time of 28.7 min in the chromatogram of the degradation product **3** from **7**.

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