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Ceriopsins A–D, diterpenoids from *Ceriops decandra*☆

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Abstract

Chemical examination of the ethyl acetate solubles of the CH_3OH:CH_2Cl_2 (1:1) extract of the roots of *Ceriops decandra* collected from Kauvery estuary resulted in the isolation of four new diterpenoids, ceriopsins A–D (**1**–**4**). The structures of the new diterpenoids were elucidated by a study of their physical and spectral data as methyl 17-hydroxy-16-oxobeyeran-18-oate (**1**), methyl 16(*R*)-16,17-dihydroxybeyeran-18-oate (**2**), 1β,15(*S*)-isopimar-7-ene-1,15,16-triol (**3**), and 8,15(*R*)-epoxypimarane-1β,16-diol (**4**). © 2002 Published by Elsevier Science Ltd.

Keywords: Indian mangrove; *Ceriops decandra*; Rhizophoraceae; New diterpenoids; Ceriopsins A–D

1. Introduction

The mangrove plants of the genus *Ceriops* (Rhizophoraceae), represented by the two species *C. decandra* (syn: *C. roxburghiana*) and *C. candolleana* (syn: *C. tagal*), are distributed along the sea coast of India and in the Andaman and Nicobar Islands (Shukla and Chandel, 1991). These plants are valued for their rich tannin content and are a rich source of pentacyclic triterpenoids (Ghosh et al., 1985), the gibberellin group of diterpenoids (Chatterjee and Chatterjee, 1979), procyanidins (Seshadri and Trikha, 1971), and α-catechin (Majumdar and Pattra, 1976). The decoction of the bark of *C. tagal* was used to treat haemorrhages and malignant ulcers (Rastogi and Mehrotra, 1991). A recent study showed that the water and alkaline extracts from the leaves of *C. decandra* possess radical modulation activity in scavenging superoxide anions produced by hypoxanthine-xanthine oxidase (Sakagami et al., 1998). In continuation of an interest on the chemical constituents of Indian mangrove plants (Anjaneyulu and Lakshmana Rao, 2000, 2001; Anjaneyulu et al., 2000, 2001a, b) we examined the plant *C. decandra* collected from the Kauvery estuary (Parangpattai coast) and report on the isolation and structural elucidation of four new diterpenoids, ceriopsins A-D (**1**–**4**), from the ethyl acetate solubles of the CH_3OH:CH_2Cl_2 (1:1) extract of the roots. The structures of the new compounds were established as, methyl 17-hydroxy-16-oxobeyeran-18-oate, ceriopsin A (**1**); methyl 16(*R*)-16,17-dihydroxybeyeran-18-oate, ceriopsin B (**2**); 1β,15(*S*)-isopimar-7-ene-1,15,16-triol, ceriopsin C (**3**); and 8,15(*R*)-epoxypimarane-1β,16-diol, ceriopsin D (**4**) by a study of their physical and spectral data. Earlier, the species was reported to afford gibberellins, but not beyerane, pimarane or isopimarane diterpenoids. Consequently, this species apparently shows great variation in its chemical constituents with place of collection.

2. Results and discussion

Ceriopsin A (**1**) was isolated as colorless needles from MeOH, mp 135–139 °C, and its molecular formula was established as $C_{21}H_{32}O_4$ from elemental analysis and EIMS, $[M]^+$ at m/z 348. It exhibited hydroxyl (3415 cm^{-1}) and carbonyl (1718 cm^{-1}) absorptions in the IR spectrum. The ^1H and ^{13}C NMR spectra of ceriopsin A are reminiscent of a beyerane skeleton (Anjaneyulu et al., 2001b). Two tertiary methyls appeared at δ 0.70 and 1.20, while the remaining two extra skeletal carbons were present as a carbomethoxyl (δ 3.64, 3H, *s*) and a hydroxymethyl at δ 3.75, 1H, *d*, $J = 11$ Hz and 3.50, 1H, *d*, $J = 11$ Hz shifted in its mono acetate **1a**, $C_{23}H_{34}O_5$, to δ 4.20, 1H, $J = 10.5$ Hz and 4.10, 1H, $J = 10.5$ Hz. Its ^{13}C NMR spectrum showed all twenty-one carbon signals,

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whose multiplicities were derived from the DEPT spectrum as 3 methyls, 10 methylenes, 2 methines, and 6 quaternary carbons. The ^{13}C signals at δ 65.0 (*t*), 177.7 (*s*) and 223.1 (*s*) confirmed the presence of hydroxymethyl, carbomethoxyl, and keto carbonyl functionalities. The keto group could be located at C-16 considering its ^{13}C value (δ 223.1), as observed in other 16-ketobeyerane derivatives (Oliveira and Starapasson, 1996), by the absence of a C-15–16 double bond, and by the HMBC correlation between C-16 (δ 223.1) and the hydroxymethylene protons, 17-H_2 at δ 3.62. This also located the hydroxymethyl group at C-13. The C-18 was taken as the carbomethoxyl group in view of the presence of only one tertiary methyl (19-H_3) at δ 28.7 at C-4. If both are tertiary methyls, C-19 and C-18 would have appeared at δ 22.3 and 33.6, respectively, as in 15(*S*)-isopimar-7-ene-15,16-diol (Subrahmanyam et al., 1999). This was confirmed by the HMBC correlation observed between the carbomethoxyl carbon (δ 177.7) and 19-H_3 at δ 1.20. The presence of a NOESY correlation between 5-H and 9-H suggested a *trans–trans* relationship between the junctions C-5-C-10 and C-10-C-9. The NOESY correlation observed between 20-H_3 and 15-H_2 indicated that the bridge-head at C-8 and C-13 is *cis* to 20-H_3 indicating the structure and relative stereochemistry of ceriopsin A as methyl 17-hydroxy-16-oxobeyeran-18-oate (**1**). The absolute configuration of ceriopsin A was assumed to be the same as beyerane in view of its negative specific rotation as found for all beyeranes (Konishi et al., 2000).

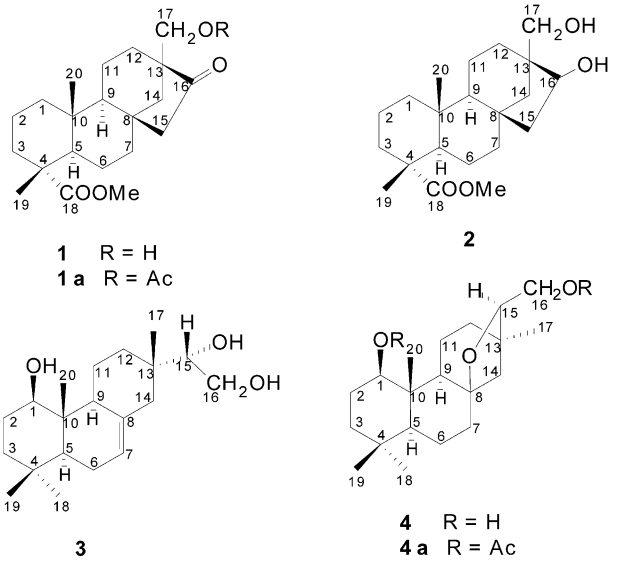
Ceriopsin B (**2**) was obtained as colorless needles from MeOH, mp 164–66 °C, and its molecular formula was established as $C_{21}H_{34}O_4$ from elemental analysis and EIMS, $[M]^+$ at *m*/*z* 350 (6%). In the IR spectrum hydroxyl (3475 and 3390 cm^{-1}) and carbonyl (1707 cm^{-1}) absorptions were displayed. The ^1H and ^{13}C NMR spectra of ceriopsin B were very similar to those of ceriopsin A, except for a difference in the functional groups. In place of a keto carbonyl in ceriopsin A, a secondary hydroxyl was present in ceriopsin B. Ceriopsin B showed a carbomethoxyl (δ 3.58, 3H, *s*) and a pair of hydroxymethylene protons at δ 3.89, 1H, *d*, $J = 10.2$ Hz and 3.81, 1H, *d*, $J = 10.2$ Hz as in ceriopsin A, and, in addition, a hydroxymethine at δ 4.88 (1H, *dd*, $J = 7.2$, 1.5 Hz). Its ^{13}C NMR spectrum confirmed the presence of the functional groups, COOMe (δ 177.8, *s*); CH_2OH (δ 68.3, *t*) and CHOH (δ 75.3, *d*) whose location was derived by the important HMBC correlations observed between C-16 (δ 75.3) and 17-H_2, 15-H_2, and 14-H_2, and the correlations between C-17 (δ 68.3) and 16-H, 12-H_2 and 14-H_2 on one side, and the correlations between C-18 (δ 177.8) and 19-H_3 and 5-H on the other side. The structure of ceriopsin B could thus be deduced as methyl 16,17-dihydroxybeyeran-18-oate (**2**).

The several NOESY correlations observed gave the relative stereochemistry of the molecule, including the configuration of the 16-hydroxyl. The 5-H showed correlation with 9-H, and the 16-H (δ 4.88) showed a positive NOESY correlation with one of the protons at C-15, i.e., 15α-H (δ 2.25), to suggest their *syn*-relationship. The 11β-H (δ 1.72) showed a positive NOESY correlation with the same 15 pro *R* proton and with 20-H_3 (δ 0.91) to suggest the configuration, though not conclusively, at C-16 as *R*. The absolute configuration of ceriopsin B was assumed to be the same as for beyerane in view of its negative specific rotation, as found for all beyeranes (Konishi et al., 2000)

Ceriopsin C (**3**) was obtained as a colorless oil and its molecular formula was assigned as $C_{20}H_{34}O_3$ from elemental analysis and EIMS, $[M]^+$ at *m*/*z* 322. The IR spectrum showed multiple hydroxyl absorptions in the hydroxylic region (3420–3410 cm^{-1}). Its ^1H NMR spectrum showed the presence of four tertiary methyls at δ 0.81 (*s*, 3H), 0.86 (*s*, 6H), 0.90 (*s*, 3H), a trisubstituted olefinic proton at δ 5.47 (1H, *brs*), and a 1,2-dihydroxyethyl substituent at δ 3.72 (1H, *dd*, $J = 10.5$, 3.0 Hz), 3.68 (1H, *dd*, $J = 9.5$, 3.0 Hz), and 3.47 (1H, *dd*, $J = 10.5$, 9.5 Hz), in addition to a secondary hydroxyl (CHOH, δ 3.43, 1H, *dd*, $J = 10.8$, 4.5 Hz). The ^1H and ^{13}C NMR spectral data of the isolate were comparable, except for the differences due to the presence of a hydroxyl in ring A, with those of a δ^7-isopimarene having a 1,2-hydroxyethyl group at C-13, as observed in 15(*S*)-isopimar-7-ene-15,16-diol isolated from the mangrove plant *Bruguiera gymnorhiza* (Subrahmanyam et al., 1999) and other related compounds (Bansal et al., 1980). It showed three oxygenated carbons at δ 81.5 (*d*), 72.7 (*d*), and 62.3 (*t*), and two olefinic carbons at δ 136.0 (*s*), and 122.1 (*d*). The C-20, in the absence of a hydroxyl group at C-1, appears around δ 15 ppm (Subrahmanyam et al., 1999), while in its presence it appears around δ 9 ppm, being a γ-carbon (Subrahmanyam et al., 1999). The appearance of C-20 at δ 8.5 in ceriopsin C suggested the presence of a hydroxyl group at C-1, and its configuration was derived as β equatorial from the coupling constants observed for the 1α-axial proton (1H, *dd*, $J = 10.8$ and 4.5 Hz). The configuration at C-15 was deduced to be *S* from its ^{13}C value δ 72.7, which is close to the value of C-15 (δ 72.9) in 15(*S*)-isopimar-7-ene-15,16-diol (Subrahmanyam et al., 1999). Thus, the structure of ceriopsin C could be derived as 1β,15(*S*)-isopimar-7-ene-1,15,16-triol (**3**). The location of the functional groups in the molecule could be confirmed by the important HMBC correlations observed between C-1 (δ 81.5) and 20-H_3, 2-H_2, and 3-H_2, and C-7 (δ 122.1) and 9-H, 5-H, 6-H_2, and 14-H_2, amongst others. The relative stereochemistry of the chiral centers for an isopimarane skeleton was revealed by the NOESY correlations between 1α-H and 9-H, 5-H and 9-H, and in particular, the correlations between 9α-H and 12α-H, and 12α-H and 14α-H with 15-H indicating 17-H_3 as β-methyl to be *cis* disposed to 20-H_3. Ceriopsin C differed

completely in its physical and spectral characteristics from an isomeric pimaranetriol, 1β,15(*R*)-*ent*-pimar-8(14)-ene-1,15,16-triol isolated very recently from *Bruguiera gymnorhiza* (Subrahmanyam et al., 1999).

Ceriopsin D (**4**) was obtained as colorless oil and the molecular formula was assigned as $C_{20}H_{34}O_3$ from elemental analysis and the FABMS $[M+1]^+$ at *m*/*z* 323. The EIMS did not show a molecular ion, but an intense peak was observed at *m*/*z* 292 [M^+-30, 80%]. Its IR spectrum showed strong hydroxyl absorption (3434 cm^{-1}). The ^1H NMR spectrum showed four tertiary methyls at δ 0.85 (*s*, 6H), 0.92 (*s*, 3H), and 1.04 (*s*, 3H), and the presence of a set of hydroxymethylene protons (–$\underline{CH_2}$OH, δ 3.37, 1H, *dd*, *J* = 10.8, 7.5 Hz and 3.48, 1H, *dd*, *J* = 10.8, 2.5 Hz) coupled to an oxymethine proton at δ 3.25 (1H, *dd*, *J* = 7.5, 2.5 Hz). It formed a diacetate, **4a**, on acetylation with pyridine/Ac_2O, $C_{24}H_{38}O_5$, in which the hydroxymethylene protons and hydroxymethine proton, on acetylation, moved downfield to δ 3.95 and 4.50, respectively as multiplets. Ceriopsin D also showed an oxymethine proton at δ 3.74 (1H, *dd*, *J* = 7.5, 2.5 Hz) which did not change on acetylation, indicating that it might be connected to a carbon with an ether oxygen. The four oxygenated carbons at δ 63.8 (*t*), 80.0 (*d*), 84.6 (*d*), and 82.7 (*s*) supported the presence of one primary and one secondary hydroxyl, and an ether linkage between a secondary and a tertiary carbon. From the above data it might be inferred that the 1,2-dihydroxyethyl group at C-13 in a pimarane or isopimarane was involved in a tetrahydrofuran bridge between C-15 and C-8. The appearance of C-20 at δ 8.4 indicated the presence of a hydroxyl group at C-1, as observed in ceriopsin C and other 1-hydroxypimarane derivatives (Subrahmanyam et al., 1999). The coupling constants of H-1 (*J* = 10.8 and 4.8 Hz) suggested its axial configuration, with the hydroxyl group at C-1 being equatorial. The configuration at C-15 was deduced to be *R* from its carbon chemical shift at δ 84.6, a value close to the value of C-15 (δ 84.7) of 8,15-oxidopimara-16,18-diol (Wenkert et al., 1979) but not to its value (δ 88.0) in the 15-*S* compound. The location of the functional groups was well-supported by the important HMBC correlations observed between C-1 (δ 80.0) and 2-H_2, 3-H_2, 5-H, and 20-H_3, and for C-15 (δ 84.6) with 16-H_2, 14-H_2, 12-H_2, and 17-H_3. The relative stereochemistry at the respective chiral centers of a pimarane skeleton was revealed by the important NOESY correlations observed between 5-H and 9-H, 5-H and 7α-H, 5-H and 1α-H, and the correlations observed between 9-H and 12α-H, 9-H and 1α-H, 9-H and 14α-H, and the correlation between 11β-H and 15-H to derive the structure of ceriopsin D as 8,15(*R*)-epoxypimarane-1β,16-diol (**4**). Three 8,15-epoxypimarane derivatives were isolated from the plant *Liatris laevigata* (Herz and Kulanthaivel, 1983) and their absolute configuration was decided as



ent-pimaranes from the (+)-ve CD curves. The absolute configuration of ceriopsin D could not be decided for want of CD data.

3. Experimental

3.1. General

Melting points were determined on a VEB-Analytic Dreader HMK hot plate and are uncorrected. IR spectra were recorded on a Perkin-Elmer-841 IR spectrometer in $CHCl_3$ solution. UV spectra were recorded on a Milton Roy Spectronic 1201 spectrometer in $CHCl_3$. ^1H NMR spectra were measured on a Bruker Advance DRX 300 and Jeol JNM EX-90 spectrometers. ^{13}C NMR spectra were measured on a Bruker Advance DRX 300 spectrometer at 75 MHz and Jeol JNM EX-90 spectrometer at 22.5 MHz using $CDCl_3$ as a solvent and tetramethylsilane as an internal reference. Optical rotations were determined on a Rudolph Autopol-III polarimeter. Elemental analyses were determined on a Carlo Erba 1108 instrument. Mass spectra were obtained on a Jeol JMS-300 spectrometer.

3.2. Plant material

The roots of *Ceriops decandra* were collected from Parangipattai coast (Latitude 11° 07′ N and Longitude 79° 50′ E), Kauvery estuary of India in March, 1999. The plant material was kindly identified by Professor B. Kondala Rao, Department of Marine Living Sources, Andhra University, Visakhapatnam. Voucher specimens (Code: AU1/182) are deposited at the Marine Museums of the School of Chemistry, Andhra University and the National Institute of Oceanography, Goa.

3.3. Extraction and isolation

The air-dried and powdered plant material (3.0 kg) was exhaustively extracted with CH_2Cl_2:MeOH (1:1). Removal of the solvent from the combined CH_2Cl_2:MeOH extracts gave a residue (60 g) which was extracted with EtOAc (5×600 ml). Removal of the solvent from the EtOAc extract under reduced pressure gave a residue (35 g). This residue was subjected to column chromatography over silica gel (Acme brand, 100–200 mesh, 350 g) using solvents of increasing polarity from *n*-hexane through EtOAc. In all, 240 fractions (800 ml) were collected. The fractions showing similar spots were combined and the residues from therein were subjected to rechromatography over silica gel or silver nitrate (20%) impregnated silica gel columns to yield ceriopsins A–D (**1**–**4**) as given below.

The residue from the column fractions 92–106 (*n*-hexane: EtOAc; 8.75:1.25) furnished ceriopsin A (**1**) (45 mg), the residue from the column fractions 126–145 (*n*-hexane: EtOAc; 8.0:2.0) furnished ceriopsin D (**4**) (50 mg), the residue from the column fractions 150–164 (*n*-hexane: EtOAc; 7.0:3.0) furnished ceriopsin B (**2**) (40 mg), the residue from the column fractions 170–185 (*n*-hexane: EtOAc; 6.5:3.5) furnished ceriopsin C (**3**) (30 mg).

*3.3.1. Ceriopsin A (**1**).* Colorless needles from MeOH, mp 135–39 °C, $[\alpha]_D^{25}$ −47.0° (*c* 0.6, $CHCl_3$). IR (Nujol) ν_{max} cm^{-1} 3415 (OH), 1718 (carbonyl). Found. C 72.25%, H 9.02%, $C_{21}H_{32}O_4$ requires C 72.41%, H 9.19%. EIMS *m*/*z*: 348 $[M]^+$, 330, 289, 271, 229, 181, 133, 121, 109, 81, 54. ^1H NMR (300 MHz, $CDCl_3$): see Table 1 and ^{13}C NMR (75 MHz, $CDCl_3$,): see Table 2.

*3.3.2. Acetylation of ceriopsin A (**1**).* Ceriopsin A (20 mg) was acetylated with a mixture of acetic anhydride (2 ml) and pyridine (2 ml) at room temperature for 24 h. After usual work up, it yielded a monoacetyl derivative **1a** (18 mg), colorless needles from MeOH, mp 125–28 °C, $[\alpha]_D^{25}$ −40.2° (*c* 0.3, $CHCl_3$). IR (Nujol) ν_{max} cm^{-1} 1728, 1242 (acetate). Found C 70.58%, H 8.52%, $C_{23}H_{34}O_5$ requires C 70.76%, H 8.71%. ^1H NMR (90 MHz, $CDCl_3$), δ 0.72, 1.22 (3H each, *s*, Me), 2.05 (3H, *s*, acetate methyl), 3.65 (3H, *s*, COOMe), 4.15 (2H, AB*q*, $J = 10.5$ Hz, 17-H_2).

Table 1
^1H NMR data of compounds **1–4**[a]

Position	**1**[b]	**2**[c]	**3**[b]	**4**[b]
1α-H	0.95 *m*	0.85 *m*	3.43 (*dd*, *J* = 10.8, 4.5)	3.25 (*dd*, *J* = 10.8, 4.8)
1β-H	1.75 *m*	1.76 *m*	–	–
2α-H	1.86 *m*	2.00 *m*	1.62 *m*	1.48 *m*
2β-H	1.46 *m*	1.42 *m*	1.25 *m*	1.58 *m*
3α-H	1.02 *m*	1.05 *m*	1.28 *m*	1.70 *m*
3β-H	2.10 *m*	2.30 *m*	1.45 *m*	1.55 *m*
5-H	1.12 *m*	1.10 *m*	1.10 *m*	1.25 *m*
6α-H	1.90 *m*	1.85 *m*	1.50 *m*	1.40 *m*
6β-H	1.72 *m*	1.75 *m*	1.96 *m*	1.60 *m*
7α-H	1.50 *m*	1.40 *m*	5.47 (br s)	1.42 *m*
7β-H	1.70 *m*	1.60 *m*	–	1.38 *m*
9-H	1.30 *m*	1.18 *m*	1.95 *m*	0.76 *m*
11α-H	1.90 *m*	2.15 *m*	2.15 *m*	1.72 *m*
11β-H	1.45 *m*	1.72 *m*	1.32 *m*	2.18 *m*
12α-H	1.30 *m*	1.60 *m*	1.26 *m*	1.32 *m*
12β-H	1.82 *m*	2.35 *m*	1.60 *m*	1.24 *m*
14α-H	1.28 *m*	1.25 *m*	1.64 *m*	1.58 *m*
14β-H	1.82 *m*	1.75 *m*	2.45 *m*	1.22 *m*
15α-H	2.65	2.25 *m*	–	3.74 (*dd*, *J* = 7.5, 2.5)
15β-H	1.85	1.90 *m*	3.72 (*dd*, *J* = 10.5, 3)	–
16-H	–	4.88 (*dd*, *J* = 7.2, 1.5)	3.47 (*dd*, *J* = 10.5, 9.5)	3.37 (*dd*, *J* = 10.8, 7.5)
			3.68 (*dd*, *J* = 9.5, 3.0)	3.48 (*dd*, *J* = 10.8, 2.5)
17-H_2	3.75 (*d*, *J* = 11)	3.89 (*d*, *J* = 10.2)	0.81 *s*	0.92 *s*
	3.50 (*d*, *J* = 11)	3.81 (*d*, *J* = 10.2)		
18-H_3	–	–	0.86 *s*	0.85 *s*
19-H_3	1.20 *s*	1.19 *s*	0.90 *s*	0.85 *s*
20-H_3	0.70 *s*	0.91 *s*	0.86 *s*	1.04 *s*
COOMe	3.64 *s*	3.58 *s*	–	–

[a] Measured at 300 mHz (the chemical shifts of the respective protons between 1.0 and 2.5 were taken from HMQC data and the multiplicities not resolved).

[b] Chemical shifts in δ from TMS (multiplicity, *J* in Hz) in $CDCl_3$.

[c] Chemical shifts in δ from TMS (multiplicity, *J* in Hz) in d_5-pyridine.

Table 2
^{13}C NMR data of compounds **1–4, 4a**

Carbon No.	**1**[a,c]	**2**[b,c]	**3**[a,c]	**4**[a,c]	**4a**[a,d]
1	39.7	40.1	81.5	80.0	82.6
2	19.7	19.3	29.6	28.8	24.9
3	37.8	38.3	40.0	38.4	38.5
4	43.7	43.9	32.7	32.5	32.9
5	56.9	57.1	50.1	55.0	54.9
6	21.6	22.3	23.2	18.8	20.4
7	41.3	42.2	122.1	39.1	39.2
8	39.6	42.5	136.0	82.7	82.6
9	55.3	56.8	52.1	54.1	54.7
10	37.9	38.5	41.2	42.6	41.9
11	18.8	20.5	23.6	22.2	21.9
12	32.0	30.2	35.5	39.3	39.6
13	54.0	48.0	36.4	40.4	41.4
14	48.9	50.8	46.0	51.8	51.9
15	48.8	43.5	72.7	84.6	82.6
16	223.1	75.3	62.3	63.8	65.7
17	65.0	68.3	22.6	19.4	21.0
18	28.7	28.8	33.2	32.9	33.2
19	13.1	13.4	22.3	21.3	21.9
20	177.7	177.8	8.5	8.4	10.1
COOMe	51.2	51.0	–	–	–
OCOCH$_3$					170.8
					170.6
OCOCH$_3$					21.9
					21.8

[a] Chemical shifts in δ from TMS taken in $CDCl_3$.
[b] Chemical shifts in δ from TMS taken in d_5-pyridine.
[c] Measured at 75 MHz.
[d] Measured at 22.5 mHz.

*3.3.3. Ceriopsin B (**2**)*. Colorless needles from MeOH, mp 164–166 °C, $[\alpha]_D^{25}$ −37.5° (*c* 0.80, $CHCl_3$). IR (Nujol) ν_{max} cm^{-1} 3475, 3390 (OH), 1707 (carbonyl). Found C 71.75%, H 9.60%, $C_{21}H_{34}O_4$ requires C 72.00%, H 9.71%. EIMS *m/z*: 350 [M]$^+$,336, 315, 301, 292, 288, 274, 260, 204, 181, 145, 121, 91, 55. ^{1}H NMR (300 MHz, d_5-pyridine,): see Table 1 and ^{13}C NMR (75 MHz, d_5-pyridine,): see Table 2.

*3.3.4. Ceriopsin C (**3**)*. Colorless oil, $[\alpha]_D^{25}$ +3.0° (*c* 0.4, $CHCl_3$). IR (Nujol) ν_{max} cm^{-1} 3420–3410 (OH), 1610, 900 (unsaturation). Found C 74.30%, H 10.40%, $C_{20}H_{34}O_3$ requires C 74.53%, H 10.56%. EIMS *m/z*: 322 [M]$^+$, 304, 291, 273, 261, 243, 187, 121, 105, 95, 55. ^{1}H NMR (300 MHz, $CDCl_3$,): see Table 1 and ^{13}C NMR (75 MHz, $CDCl_3$,): see Table 2.

*3.3.5. Ceriopsin D (**4**)*. Colorless oil, $[\alpha]_D^{25}$ +50.6° (*c* 1.5, $CHCl_3$). IR (Nujol) ν_{max} cm^{-1} 3434 (OH); Found C 74.40%, H 10.34%, $C_{20}H_{34}O_3$ requires C 74.53%, H 10.56%. (+)ve FABMS *m/z*: 323 [M+H]$^+$, 305, 291, 273, 257, 245, 105. ^{1}H NMR (300 MHz, $CDCl_3$): see Table 1 and ^{13}C NMR (75 MHz, $CDCl_3$): see Table 2.

*3.3.6. Acetylation of ceriopsin D (**4**)*. Ceriopsin D (30 mg) was acetylated with a mixture of acetic anhydride (2 ml) and pyridine (2 ml) at room temperature for 24 h. After usual work up, it yielded a monoacetyl derivative **4a** (25 mg), colorless oil, $[\alpha]_D^{25}$ +43.5° (*c* 0.4, $CHCl_3$). IR (Nujol) ν_{max} cm^{-1}, 1739, 1244. Found C 70.72%, H 9.18%, $C_{24}H_{38}O_5$ requires C 70.93%, H 9.36%. ^{1}H NMR (90 MHz, $CDCl_3$,): δ 0.85, 0.85, 0.98, 1.18 (3H each, *s*, Me), 2.05 (3H, *s*, acetate methyl), 2.10 (3H, *s*, acetate methyl), 3.74 (1H, *dd*, *J*=7.5, 2.5 Hz, 15-H), 3.95 (1H, *m*, 1-H), 4.50 (1H, *m*, 16-H) and ^{13}C NMR (22.5 MHz, $CDCl_3$): see Table 2.

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