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SCALARANE-TYPE BISHOMOSESTER TERPENES FROM THE SPONGE *PHYLLOSPONGIA FOLIASCENS*

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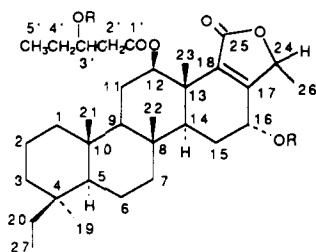
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ABSTRACT.—Five new 20,24-bishomoscalarane sesterterpenes, phyllactones A [1], B [2], C [3], D [4], and E [5], are reported from the sponge *Phyllospongia foliascens* collected in the waters of the Nansha Islands in the South China Sea. Structural elucidation of these compounds is based on spectral data and chemical conversions. Phyllactones A and B show moderate cytotoxicity against KB cells (IC₅₀ 20 µg/ml).

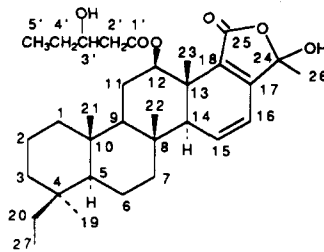
The sponge *Phyllospongia* (syn. *Carteriospongia*) *foliascens* Pallas (Spongiidae) has proved to be a rich source of 20,24-bishomoscalarane sesterterpenes (1–8). During the course of our investigation of Chinese marine organisms, we have reported (1,2) recently the isolation and structure elucidation of four sesterterpenes belonging to this group from the sponge *P. foliascens* collected from the Xisha islands in the South China Sea. Further investigation of the sponge *P. foliascens* collected from the Nansha islands has led to the isolation and characterization of five new 20,24-bishomoscalarane sesterterpenes, named phyllactones A–E. Interestingly, the sesterterpene metabolites of *P. foliascens* collected from two localities differ in the relative stereochemistry of the substituents at C-12 and C-16.

RESULTS AND DISCUSSION

Phyllactone A [1] was obtained as fine needles from Me₂CO, mp 193–194°, [α]_D 11° (c = 1.13, CHCl₃). The molecular formula C₃₂H₅₀O₆ was deduced from the cims peak at *m/z* 531 [MH]⁺ and ¹³C data. Phyllactone A belongs to the 20,24-bishomoscalarane sesterterpene group indicated by eims at *m/z* 219 and 205 which are common fragment ions of the 20,24-bishomoscalarane sesterterpenes due to fragmentation across the C ring (5), and the ¹H-nmr spectrum which showed four methyl singlets at δ 0.80, 0.86, 0.90, and 1.20 and one methyl triplet at δ 0.75 typical of 20,24-bishomoscalarane derivatives (1–8). Resonances in the ¹³C-nmr spectrum at δ 170.3 (s), 162.4 (s), 137.1 (s), 78.3 (d) and 19.6 (q) together with signals in the ¹H-nmr spectrum at δ 4.83 (q, 6.5 Hz) and 1.51 (d, 6.5 Hz) demonstrated the presence of a 2,3,4-trisubstituted butenolide function (1,7,9). This suggestion was also supported by absorption in the ir spectrum of 1 at 1722 cm⁻¹ and uv maximum at 211 nm. The ¹³C-nmr (Table 3) and ¹H-nmr (Table 1) data of phyllactone A showed the presence of a 3-hydroxypentanoyl residue (3,4). ¹H-¹H COSY showed correlation between the resonance at δ 2.56 (H-2') and the signal at δ 4.03 assigned as H-3', which was further correlated to a signal at δ 1.52 (H-4'). The latter signal was correlated to a methyl triplet at δ 0.96 (H-5'). The existence of the 3-hydroxypentanoyl residue was supported by the long range heteronuclear scalar correlations H-2'/C-1' and H-2'/C-3' as well as H-5'/C-3' and H-5'/C-4', and further substantiated by cims at *m/z* 413 [M - CH₃CH₂CH(OH)CH₂COO]⁺ and 101 [CH₃CH₂CH(OH)CH₂CO]⁺. Ir absorption at 1751 cm⁻¹ was also consistent with the presence of an acyl group. The remaining two downfield ¹H-nmr signals, a doublet of doublets (*J* = 11, 4 Hz) at δ 5.04 and a doublet (*J* = 3.5 Hz) at δ 4.41, were assigned to the protons of two oxymethines CH-12 and CH-16. The associated carbons resonated at δ 76.4 and 63.0, respectively.



- 1** R=H, Me-26 α
2 R=H, Me-26 β
3 R=Ac, Me-26 β
6 R=Ac, Me-26 α



- 4** Me-26 α
5 Me-26 β

The structure **1** was further established by extensive nmr studies, including ^1H - ^1H COSY, ^1H - ^{13}C COSY, HMBC (10), and NOESY (11) experiments, and detailed comparison of the ^1H - and ^{13}C -nmr data with those of scalarane-type sesterterpenes (1–8).

The location of the 3-hydroxypentanoyl residue was assigned to C-12 by ^1H - ^1H COSY and HMBC spectra. The ^1H - ^1H COSY spectrum showed correlation between the signal at δ 5.04 (H-12) and resonances at δ 1.80 (H-11 β) and 1.55 (H-11 α). The latter signals were correlated to each other and in turn correlated to a signal at δ 1.10 (H-9 α). The long range H/C correlation between H-12 and C-1' (δ 173.0) further supported the C-12 location for the acyl group. The observed coupling constant for H-12 ($J = 11, 4$ Hz) indicated an H-12 α stereochemistry, and this was also confirmed by a NOESY correlation between H-12 α and H-9 α . The remaining hydroxy group in **1** was

TABLE 1. Nmr Data for Compound **1**.^a

Position	δ H	^1H - ^{13}C ^b	NOESY
7 α	0.96 m		14 α , 15 α
7 β	1.80 m		15 β
9 α	1.10 m		11 α , 12 α
11 α	1.55 m	8, 9, 12	9 α , 12 α
11 β	1.80 m	8, 9, 12	22, 23
12 α	5.04 dd, 11, 4	1', 18, 23	9 α , 11 α
14 α	1.54 m		15 α
15 α	1.80 m	8, 16	7 α , 14 α
15 β	1.88 m	8, 14, 16, 17	7 β , 16 β , 23
16 β	4.41 d, 3.5	14, 17	15 β , 24 β
19	0.80 s		
20a	1.18 m	5, 19, 27	21
20b	1.58 m	19	
21	0.86 s		20a
22	0.90 s		11 β , 23
23	1.20 s	18	11 β , 22
24 β	4.83 q, 6.5	17, 18	16 β , 26
26	1.51 d, 6.5	17, 24	24 β
27	0.75 t, 7		
2'	2.56 m	1', 3'	3', 5'
3'	4.03 m		2', 4', 5'
4'	1.52 m		2', 3'
5'	0.96 t, 7	3', 4'	2', 3'

^aSpectra were recorded in CDCl_3 on a 400 MHz instrument.

^bThe correlations were obtained from HMBC.

assigned to C-16 in ring D on the basis of ^1H - ^1H COSY; this was substantiated by long range correlations between H-16 and C-17 together with C-14. The small coupling constant for H-16 ($J = 3.5$ Hz) revealed a 16α -OH stereochemistry.

As reported (7), the orientation of the butenolide was determined by the observed long range ^1H - ^{13}C correlations between H-15, H-26, and one of the sp^2 carbons (δ 162.4) assigned as the β carbon of the α,β -unsaturated carbonyl system. The other sp^2 carbon (δ 137.1) was in turn correlated to H-12 and H-23. The α configuration assigned to Me-26 was based on a NOESY correlation between H-16 and H-24.

By comparison of the ^{13}C data of **1** with those of related 20,24-bishomoscalarane sesterterpenes (1-8), the β configuration was assigned to the C-4 ethyl group, since its methylene carbon signal is at δ 24.6 in good agreement with the shifts determined for this carbon in related C-4 α -ethyl homosesterterpenes. Furthermore, the chemical shift of C-19 at δ 28.6 can only be accounted for by an equatorial methyl group in accordance with the well-known assignments of C-4 gem dimethyl units of other scalarane sesterterpenes (12) and triterpenes (13-15). The assignment of the C-19 resonance was confirmed by the long range heteronuclear correlations observed between C-19 and H_a -20 and H_b -20. An nOe between H-20 and H-21 in the NOESY spectrum further supported the β ethyl configuration at C-4. Hence the structure of phyllactone A was determined as **1**.

Phyllactone B [**2**] was obtained as fine needles, mp 179-180 $^\circ$, $[\alpha]_{\text{D}} + 27^\circ$ ($c = 0.98$, CHCl_3). A cims peak at m/z 531 $[\text{MH}]^+$ and ^{13}C data showed the molecular formula of **2** to be $\text{C}_{32}\text{H}_{50}\text{O}_6$, the same as **1**. The ir spectrum showed bands at 3511 (br, hydroxyls), 1749 (acyl), 1712 (α,β -unsaturated- γ -lactone) cm^{-1} . The uv absorption at 216 nm was compatible with the presence of an α,β -unsaturated γ lactone (1,7,9). The ^1H -nmr spectrum contained four methyl singlets at δ 0.80, 0.88, 0.91, and 1.16, a methyl doublet at δ 1.38 ($J = 6.5$ Hz), and two methyl triplets at δ 0.75 ($J = 7$ Hz) and 0.96 ($J = 7$ Hz). Other prominent features in the ^1H -nmr spectrum were one doublet of doublet at δ 5.00 ($J = 11, 4$ Hz) assigned to H-12, one doublet at δ 4.39 ($J = 3.5$ Hz) assigned to H-16, one quartet at δ 5.03 ($J = 6.5$ Hz) assigned to H-24, one multiplet at δ 4.03, and one two-protons multiplet at δ 2.54. All the above data as well as ^{13}C (Table 3) and cims data of phyllactone B strongly indicated that phyllactone B is an isomer of phyllactone A differing in the 24-methyl configuration. In particular, all the carbon chemical shifts of **2** were within 1 ppm of those of **1** with the exception of C-16, C-17, C-24, and C-26 as anticipated for C-24 epimers. Hence the structure of phyllactone B was assigned as **2**. The ^1H (δ 1.38, d) and ^{13}C (δ 18.5) data for the 24-methyl group are compatible with those of similar scalarane derivatives with 24 β -methyl groups (1,7,9). An nOe observed between H-16 and H-26 further supported the 24 β -methyl configuration.

Phyllactone C [**3**] was obtained as a gum, $[\alpha]_{\text{D}} + 29^\circ$ ($c = 0.22$, CHCl_3). Its ir spectrum showed three ester bands at 1755 (acyl), 1736 (OAc), and 1712 (α,β -unsaturated γ -lactone) cm^{-1} . No hydroxyl absorption was apparent from ir spectrum. Compound **3** had a cims peak at m/z 615 $[\text{MH}]^+$ indicating two extra acetyl groups when compared to that of **1** and **2**. This was supported by two downfield methyl singlets at δ 2.03 and 2.10 in the ^1H -nmr spectrum. The ^1H -nmr spectrum of **3** was very similar to that of **1** and **2** except for H-16, H-24, H-3', and H-2' attributed to the introduction of the acetyl groups. The similarity of the chemical shift of the methyl group assigned to C-24 position with that of **2** led us to conclude that phyllactone C [**3**] is a diacetate of phyllactone B. In order to confirm the structure of **3**, phyllactones A [**1**] and B [**2**] were subjected to acetylation with pyridine/ Ac_2O at room temperature. Both **1** and **2** gave diacetates easily. The spectral data of the diacetate of phyllactone B were found to be identical with those of **3**. Thus, the structure of phyllactone C was confirmed as **3**.

TABLE 2. ¹H-nmr Data of Compounds 2-6^a.

Proton	Compound				
	2	3	4 ^b	5 ^b	6
H-9	0.97 m ^c				
H-11	1.82 m ^c	1.76 m ^d			
	1.53 m ^c	1.52 m ^d			
H-12	5.00 dd, 11, 4	4.99 dd, 11, 4	5.18 dd, 11, 4	5.22 dd, 11, 4	4.99 dd, 11, 4
H-14	1.53 m ^c				
H-15	1.88 m ^c	1.85 m ^d	6.31 dd, 10, 3.5	6.35 dd, 10, 3.5	
H-16	4.39 d, 3.5	5.45 d, 3.5	6.41 dd, 10, 2	6.45 dd, 10, 2	5.50 d, 3.5
H-19	0.80 s	0.80 s	0.80 s	0.83 s	0.80 s
H-20	1.50 m ^c	1.58 m ^d			
	1.17 m ^c	1.16 m ^d			
H-21	0.88 s	0.84 s	0.85 s	0.85 s	0.84 s
H-22	0.91 s	0.88 s	1.03 s	1.03 s	0.88 s
H-23	1.16 s	1.18 s	1.08 s	1.08 s	1.21 s
H-24	5.03 q, 6.5	4.77 q, 6.5			4.75 q, 6.5
H-26	1.38 d, 6.5	1.39 d, 6.5	1.64 s	1.55 s	1.31 d, 6.5
H-27	0.75 t, 7	0.75 t, 7	0.75 t, 7	0.75 t, 7	0.74 t, 7
H-2'	2.54 m ^c	2.80 dd, 16, 9	2.47 m	2.47 m	2.79 dd, 16, 9
		2.65 dd, 16, 4			2.65 dd, 16, 4
H-3'	4.03 m	5.34 m	4.03 m	4.03 m	5.34 m
H-4'	1.52 m ^c	1.64 m ^d			
H-5'	0.96 t, 7	0.91 t, 7	0.96 t, 7	0.97 t, 7	0.92 t, 7
OAc		2.10 s			2.12 s
OAc		2.03 s			2.02 s

^aSpectra were recorded in CDCl₃ on a 400 MHz instrument.

^bThe data between two columns may be reversed.

^cThese data were obtained from DQF ¹H-¹H COSY.

^dThese data were obtained from decoupling experiments.

The mixture of phyllactones D [4] and E [5], obtained as needles, had a cims peak at *m/z* 529 [MH]⁺, indicating they had two fewer protons than compounds 1 and 2. This mixture exhibited only one spot on hptlc and could not be purified by hplc. The ratio between 4 and 5 was estimated to be approximately 1:1 from the integration in the ¹H-nmr spectrum. Compounds 4 and 5 possess the same 3-hydroxypentanoyl residue as phyllactones A [1] and B [2] indicated by ir bands at 1751 and 3362 cm⁻¹, and cims at *m/z* 411 [M - CH₃CH₂CH(OH)CH₂COO]⁺ and 101 [CH₃CH₂CH(OH)CH₂CO]⁺. The ¹H- and ¹³C-nmr data (Tables 2 and 3, respectively) of the 3-hydroxypentanoyl moiety were consistent with those of 1 and 2. The location of the 3-hydroxypentanoyl group at C-12 and the 12 β configuration were based on the ¹H-nmr data (Table 2) and biogenetic relationship.

In arguments similar to the ones applied in the structure elucidation of 1-3, a butenolide moiety was also suggested for phyllactones D [4] and E [5]. The remaining hydroxy group was located at C-24 in place of H-24 on this carbon based on the disappearance of the H-24 signal present in compounds 1-3 and the appearance of a ¹³C-nmr signal at δ 103.1 whose low field resonance is characteristic for a ketal. The ¹H and ¹³C nmr indicated clearly (Tables 2 and 3) that 4 and 5 are a pair of epimeric isomers at C-24. A pair of doublets of doublets at δ 6.30-6.45 were attributed to the olefinic protons H-15 and H-16. This suggestion was further supported by ¹³C-nmr data, δ 139.6 (d) and 119.6 (d) for 4; δ 139.3 (d) and 119.3 (d) for 5. The existence of Δ¹⁵ was also confirmed by uv absorption at 291 nm and ¹³C-nmr data of C-17, C-18, and C-25 (Table 3). Such a double bond extending the conjugation gives rise to a longer wavelength uv

TABLE 3. ^{13}C -nmr Data of Compounds 1, 2, 3, 4, and 5^a.

Carbon	Compound				
	1	2	3	4 ^b	5 ^b
C-1	40.2	40.5	40.3	40.1	40.5
C-2	18.3	18.1	18.3	17.9	17.9
C-3	36.8	36.7	36.8	36.8	36.8
C-4	36.2	36.2	36.3	36.3	36.3
C-5	58.7	58.5	58.7	58.8	58.8
C-6	18.3	18.3	18.3	18.3	18.3
C-7	42.0	41.9	41.9	42.2	41.0
C-8	37.6	37.5	37.6	37.0	37.0
C-9	58.2	58.0	58.2	58.5	58.5
C-10	36.8	36.7	36.9	37.6	37.6
C-11	25.1	24.9	24.3	24.3	24.4
C-12	76.1	76.0	75.7	75.1	75.8
C-13	42.0	41.2	41.3	42.4	41.1
C-14	50.1	50.1	50.6	57.2	57.0
C-15	27.6	27.4	27.3	139.6	139.3
C-16	63.0	61.1	63.3	119.6	119.3
C-17	162.4	163.9	160.1	158.6	158.2
C-18	137.1	136.6	139.0	132.1	132.1
C-19	28.6	28.6	28.6	28.9	28.7
C-20	24.6	24.7	24.6	24.7	24.7
C-21	16.8	16.8	16.9	16.8	16.8
C-22	17.5	17.2	17.2	18.9	18.9
C-23	15.1	16.0	15.7	12.7	12.7
C-24	78.3	76.2	75.8	103.1	103.1
C-25	170.3	170.5	169.3	168.6	167.9
C-26	19.6	18.5	18.3	24.1	24.2
C-27	8.7	8.7	8.7	8.8	8.8
C-1'	173.0	172.9	170.2	173.5	172.9
C-2'	42.2	42.2	41.9	42.5	42.2
C-3'	69.5	69.5	71.7	69.9	69.7
C-4'	29.7	29.7	29.8	29.6	29.6
C-5'	10.0	10.0	9.5	10.0	10.1
OAc			170.5		
			21.3		
			170.5		
			21.1		

^aSpectra were recorded in CDCl_3 at operating frequency of 62.5 MHz.^bThe data between two columns may be reversed.

absorption and causes the chemical shifts of C-17, C-18, and C-25 to move downfield. Therefore, phyllactones D and E were identified as 4 and 5.

Phyllactones A [1] and B [2] show moderate cytotoxicity against KB cells (IC_{50} 20 $\mu\text{g}/\text{ml}$).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points (uncorrected) were determined on a Buchi Apparatus. Optical rotations were measured with a Perkin-Elmer 241 polarimeter in CHCl_3 . Uv spectra were recorded on a Shimadzu UV-161 uv-visible spectrophotometer; ir on a Nicolet 205 FT-IR spectrometer; eims (70 eV) on a Kratos MS 50; cims on a Kratos MS 80 spectrometer, and nmr on Bruker AC 250 and AC 400. All nmr spectra were recorded in CDCl_3 with TMS as internal standard. All solvents used were analytical grade. Petroleum ether refers to the 60–90° fraction. Tlc grade Si gel H was used for vlc and flash cc. Preparative tlc was performed with Si gel 60 F₂₅₄. Preparative hplc was carried out by using μ -Porasil SiO_2 (7.8 mm \times 25 cm) column with uv detection.

BIOLOGICAL MATERIAL.—The sponge *P. foliascens* was collected in the waters of Chinese Nansha Islands in June 1990, and was identified by Dr. Jinhe Li, Institute of Oceanology, Qingdao, People's Republic of China. A voucher specimen has been deposited in the Research Centre of Organic Natural Products, Zhongshan University.

EXTRACTION AND ISOLATION.—The sun-dried specimens (dry wt ca. 800 g) were repeatedly extracted with MeOH at room temperature. The MeOH extract was concentrated under reduced pressure and partitioned between EtOAc-petroleum ether (1:4) and H₂O. The organic fraction was separated and dried over anhydrous Na₂SO₄. Evaporation of the solvent yielded a viscous oil (54 g) that was subjected to vlc on Si gel. Elution with varying proportions of petroleum ether/EtOAc (0–100% EtOAc) yielded 9 fractions. Repeated flash chromatography of the fourth (15% EtOAc in petroleum ether), fifth (20% EtOAc in petroleum ether), and seventh (30–40% EtOAc in petroleum ether) fractions afforded **3** (4 mg), a 1:1 mixture of **4** and **5** (38 mg), and a mixture of **1** and **2**, respectively. Compounds **1** (26 mg) and **2** (23 mg) were further purified by hplc with Et₂O as eluent.

Phyllactone A [1].—Needles from Me₂CO: mp 193–194°; [α]_D+11 (c = 1.13, CHCl₃); uv λ max 211 nm (ϵ = 7028, MeOH); ir (CHCl₃) ν max cm⁻¹ 3515 (br, OH), 1751 (ester), 1722 (α,β -unsaturated- γ -lactone); cims m/z (% rel. int.) 429 (25), 413 (98), 395 (100), 219 (23), 205 (75), 149 (58), 137 (50), 123 (48), 109 (48); cims m/z (% rel. int.) [MH]⁺ 531 (100), 515 (6), 513 (10), 501 (6), [M - CH₃CH₂CH(OH)CH₂CO]⁺ 429 (29), [M - CH₃CH₂CH(OH)CH₂COO]⁺ 413 (58), [M - OH - CH₃CH₂CH(OH)CH₂COO]⁺ 396 (31), 119 (100), (20), 101 (45); ¹H nmr see Table 1; ¹³C nmr see Table 3.

Phyllactone B [2].—Needles from Me₂CO: mp 179–180°; [α]_D+27 (c = 0.98, CHCl₃); uv λ max 216 nm (ϵ = 8494, MeOH); ir (CHCl₃) ν max cm⁻¹ 3501 (br, OH), 1749 (ester), 1712 (α,β -unsaturated- γ -lactone); cims m/z (% rel. int.) 531 (76), 429, 413 (100), 396 (44), 329 (56), 119 (44), 101 (28); ¹H nmr see Table 2; ¹³C nmr see Table 3.

Phyllactone C [3].—The compound was obtained as a gum: [α]_D+29 (c = 0.22, CHCl₃); uv λ max 220 nm (ϵ = 6182, MeOH); ir (CHCl₃) ν max cm⁻¹ 1755 (ester), 1736 (OAc), 1712 (α,β -unsaturated- γ -lactone); cims m/z (% rel. int.) [MH]⁺ 615 (100), [M - OAc]⁺ 555 (8), [M - HOAc]⁺ 554 (22), 453 (5), 410 (6), 394 (17), 378 (20), 161 (95), 143 (12); ¹H nmr see Table 2; ¹³C nmr see Table 3.

Phyllactones D [4] and E [5].—Needles from MeOH: uv λ max (MeOH) 291 nm (ϵ = 5926), 204 nm (ϵ = 5798); ir (CHCl₃) ν max cm⁻¹ 3362 (br, OH), 1751 (ester), 1710 (α,β -unsaturated γ -lactone); cims m/z (% rel. int.) [MH]⁺ 529 (100), 513 (8), 511 (12), [M - CH₃CH₂CH(OH)CH₂COO]⁺ 411 (43), 393 (45), 367 (55), 119 (82), 101 (53); ¹H nmr see Table 2; ¹³C nmr see Table 3.

ACETYLATION OF 1.—A mixture of **1** (5.0 mg), Ac₂O (150 μ l), and pyridine (150 μ l) was kept at room temperature overnight and worked up as usual (3). Diacetate **6** of phyllactone **A** was obtained as an oil (5.6 mg) after preparative tlc on Si gel plate. [α]_D+12 (c = 0.42, CHCl₃); cims m/z (% rel. int.) [MH]⁺ 615 (100), [M - OAc]⁺ 555 (45), [M - HOAc]⁺ 554 (100), 453 (16), 410 (15), 394 (96), 378 (60), 161 (100), 143 (8); ¹H nmr see Table 2.

ACETYLATION OF 2.—A solution of **2** (8.0 mg) in Ac₂O (200 μ l) and pyridine (200 μ l) was kept at room temperature overnight. Preparative tlc of the reaction mixture after usual workup yielded the diacetate of phyllactone **B** as a gum (8.8 mg) whose uv, ir, cims, and ¹H nmr were identical with those of phyllactone **C** [3].

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LITERATURE CITED

1. L. Zeng, X. Fu, J. Su, E.O. Pordesimo, S.C. Traeger, and F.J. Schmitz, *J. Nat. Prod.*, **54**, 421 (1991).
2. L. Zeng, X. Fu, J. Su, S. Chen, and J.K. Snyder, *Chem. Research Chinese Univ.*, **7**, 100 (1991).
3. H. Kikuchi, Y. Tsukitani, I. Shimizu, M. Kobayashi, and I. Kitagawa, *Chem. Pharm. Bull.*, **31**, 552 (1983).
4. I. Kitagawa, M. Kobayashi, N.K. Lee, Y. Oyama, and Y. Kyogoku, *Chem. Pharm. Bull.*, **37**, 2078 (1989).
5. J.C. Braekman, D. Daloz, M. Kaisin, and B. Moussiaux, *Tetrahedron*, **41**, 4603 (1985).
6. J.C. Braekman, D. Daloz, M. Kaisin, and B. Moussiaux, *Tetrahedron*, **42**, 445 (1986).
7. P.E. Barron, R.J. Quinn, and D.J. Tucker, *Aust. J. Chem.*, **44**, 995 (1991).

8. R.J. Quinn and D.J. Tucker, *Aust. J. Chem.*, **42**, 751 (1989).
9. K.D. Craft, E.L. Ghisalberti, B.W. Skelton, and A.H. White, *J. Chem. Soc., Perkin Trans. 1*, 155 (1983).
10. A.F. Barrero, E.A. Manzaneda, R.S. Arseniyadis, and E. Guitter, *Tetrahedron*, **46**, 8161 (1990).
11. G. Bodenhausen, H. Kogler, and R.R. Ernest, *J. Magn. Reson.*, **58**, 370 (1984).
12. P. Crews and S. Naylor, *Prog. Chem. Org. Nat. Prod.*, **48**, 203 (1985).
13. S. Seo, Y. Tomita, and K. Tori, *Tetrahedron Lett.*, **16**, 7 (1975).
14. H. Beierbeck, J.K. Saunders, and J.W. Apsimon, *Can. J. Chem.*, **55**, 2813 (1977).
15. F. Wehrli and T. Nishida, *Fortschr. Chem. Org. Naturst.*, **36**, 1 (1979).

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