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Phomadecalins A−D and Phomapentenone A: New Bioactive Metabolites from *Phoma* sp. NRRL 25697, a Fungal Colonist of *Hypoxylon* Stromata

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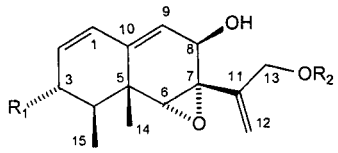
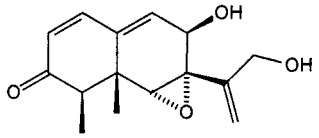
Five new natural products, phomadecalins A−D (**1**−**4**) and phomapentenone A (**5**), have been obtained from cultures of *Phoma* sp. (NRRL 25697), a fungal colonist isolated from the stromata of *Hypoxylon* sp. The structures of these compounds were elucidated through a series of 1D and 2D NMR experiments. Compounds **1**−**4** display activity against Gram-positive bacteria.

As part of our continuing search for new bioactive agents from mycoparasitic and fungicolous fungi that colonize long-lived fungal physiological structures,[1−4] we have begun to investigate mycoparasites and fungal antagonists from stromata and basidiocarps of wood decay fungi. In the course of this work, an isolate of *Phoma* sp. (NRRL 25697; mitosporic fungi) was obtained from a field-collected *Hypoxylon* stroma. Chemical investigation of cultures of this isolate led to the isolation of five new metabolites that we named phomadecalins A−D (**1**−**4**) and phomapentenone A (**5**). Details of the isolation, structure elucidation, and biological activities of these compounds are presented here.



1 $R_1 = R_2 = H$
2 $R_1 = OH$; $R_2 = Ac$
4 $R_1 = OH$; $R_2 = H$



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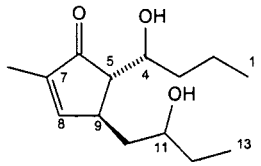

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The combined EtOAc extracts of solid-substrate fermentation cultures were fractionated sequentially by silica gel VLC, Sephadex LH-20 column chromatography, and reversed-phase HPLC to afford phomadecalins A−D (**1**−**4**) and phomapentenone A (**5**). The molecular formula of phomadecalin A (**1**) was determined to be $C_{15}H_{20}O_3$ (six degrees of unsaturation) on the basis of FABMS and NMR data. Analysis of ^{1}H and ^{13}C NMR data (Tables 1 and 2) for phomadecalin A revealed the presence of two methyl groups, two sp^3 methylene units (one oxygenated), three sp^3 methine units (two oxygenated), and two nonprotonated sp^3 carbons (one oxygenated), as well as six sp^2 carbons corresponding to 1,1-disubstituted, 1,2-disubstituted, and trisubstituted olefin units. These signals, together with two exchangeable protons, accounted for the molecular formula and required phomadecalin A (**1**) to be tricyclic.

Two continuous proton spin-systems corresponding to the C1−C4 (including C-15) and C8−C9 subunits of structure **1** were established by homonuclear decoupling experiments and were confirmed and extended by selective INEPT experiments optimizing for $J_{CH} = 4$ Hz. Irradiation of H-1 resulted in polarization transfer to C-5, C-9, and C-10, while irradiation of H-9 resulted in polarization transfer to C-1, C-5, and C-7. These results indicated that the C1−C2 and C9−C10 double bonds form a conjugated system. They also required that C-5 be directly attached to C-10 and that C-8 must be directly attached to quaternary carbon C-7 (δ_C 64.2). Selective INEPT correlations of H_3-14 to C-4, C-5, C-6, and C-10 confirmed the linkage of C-5 to C-10 and led to the connection of both C-4 and oxymethine carbon C-6 (δ_C 67.1) to C-5. Selective INEPT correlations of isolated proton H-6 to C-7 and C-11 permitted the completion of the decalin system and required connection of C-7 to olefinic carbon C-11. Irradiation of the sp^2 methylene protons at δ_H 5.33 and 5.30 (H_2-12) resulted in polarization transfer to C-7, C-11, and oxymethylene carbon C-13, indicating that C-13 is connected to the C11−C12 double bond at C-11. The molecular formula for phomadecalin A (**1**) requires the presence of an additional ring and two exchangeable protons. On the basis of the chemical shifts of C-6 (δ_C 67.1), C-7 (δ_C 64.2), and H-6 (δ_H 3.18), a C6−C7 epoxide moiety was assigned, requiring C-8 and C-13 to bear free hydroxy groups. Thus, the structure of phomadecalin A was established as shown in **1**. All NMR assignments were fully consistent with literature values for the structurally similar known compound phomenone[5] and its synthetic analogue 8-β-hydroxyphomenone.[6] Phomenone was originally reported by other workers as a phytotoxic metabolite of *Phoma exigua*.[5]

Phomadecalin B (**2**) was assigned the molecular formula $C_{17}H_{22}O_5$ (seven degrees of unsaturation) on the basis of FABMS and NMR data (Tables 1 and 2). Analysis of ^{1}H and ^{13}C NMR data revealed the presence of the same structural features found in phomadecalin A (**1**), except that the C-3 allylic methylene unit was replaced by an

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Table 1. ^{1}H NMR Data for Phomadecalins A−D (**1**−**4**) in $CDCl_3$

	δ_H (mult., *J* in Hz)			
pos.	phomadecalin A (**1**)	phomadecalin B (**2**)	phomadecalin C (**3**)	phomadecalin D (**4**)[a]
1	5.95 (br d, 9.6)	5.99 (br dd, 9.6, 2.7)	6.87 (br d, 10)	5.90 (br dd, 9.9, 2.1)
2	5.72 (br dd, 9.6, 5.1)	5.74 (br dd, 9.6, 2.4)	5.95 (br d, 10)	5.63 (br d, 9.9)
3a	2.10 (ddd, 13, 13, 5.1)	3.94 (br d, 9.0)		3.82 (br d, 10)
3b	1.88 (m)			
4	1.90 (m)	1.72 (m)	2.84 (q, 6.6)	1.64 (m)
5				
6	3.18 (s)	3.11 (s)	3.17 (s)	3.17 (s)
7				
8	4.71 (br s)	4.68 (br s)	4.84 (br d, 2.1)	4.64 (br s)
9	5.25 (br d, 2.4)	5.36 (br d, 2.4)	5.80 (br d, 2.1)	5.23 (br s)
10				
11				
12	5.33 (br d, 0.9); 5.30 (br s)	5.44 (br s); 5.36 (br s)	5.37 (br s); 5.35 (br s)	5.23 (br s); 5.19 (br s)
13a	4.31 (dd, 13, 0.9)	4.80 (br d, 13)	4.35 (br d, 13)	4.17 (br d, 13)
13b	4.18 (br d, 13)	4.70 (br d, 13)	4.22 (br d, 13)	4.04 (br d, 13)
14	0.95 (s)	0.97 (s)	1.06 (s)	0.89 (s)
15	1.03 (d, 6.8)	1.21 (d, 6.6)	1.22 (d, 6.6)	1.10 (d, 6.9)
CH_3CO		2.10 (s)		

[a] Recorded in $CDCl_3$−CD_3OD (4:1).

Table 2. ^{13}C NMR Data for Phomadecalins A−D (**1**−**4**) in $CDCl_3$

	δ_C			
pos.	phomadecalin A (**1**)	phomadecalin B (**2**)	phomadecalin C (**3**)	phomadecalin D (**4**)[a]
1	127.9	128.7	144.1	127.9
2	128.7	131.6	129.7	131.6
3	31.6	71.4	199.3	70.4
4	32.7	41.9	46.6	40.9
5	37.2	38.7	41.8	38.4
6	67.1	67.1	67.0	66.5
7	64.2	64.1	64.6	64.7
8	67.4	66.1	67.2	66.1
9	120.7	122.8	127.0	122.3
10	139.5	138.5	144.1	138.1
11	146.1	140.9	144.9	145.6
12	115.6	117.0	116.4	114.0
13	64.1	64.8	64.0	62.6
14	15.8	16.7	18.1	16.1
15	14.9	10.7	7.3	10.1
CH_3CO		20.9/170.5		

[a] Recorded in $CDCl_3$−CD_3OD (4:1).

oxygenated methine unit (δ_H/δ_C 3.92/71.4). The location of this change was confirmed by a homonuclear decoupling experiment. The NMR data also suggested the presence of an acetate unit (δ_C 20.9/170.5; δ_H 2.10). The oxymethylene protons (H_2-13) were both shifted ca. 0.5 ppm downfield relative to their positions in phomadecalin A (δ_H 4.80 and 4.60 vs δ_H 4.31 and 4.18), indicating that the oxygen attached to C-13 is acetylated in phomadecalin B.

The elemental composition of phomadecalin C (**3**) was established as $C_{15}H_{18}O_4$ (seven degrees of unsaturation) based on FABMS and NMR data. The ^{1}H and ^{13}C NMR spectra of phomadecalin C are similar to those of **1** and **2**, but detailed analysis revealed a few differences. The chemical shifts of H-1 and H-9 in **3** (δ_H 6.87 and 5.80) are significantly downfield relative to the corresponding signals in **1** and **2**. The corresponding ^{13}C NMR shifts were also downfield-shifted. Analysis of ^{13}C NMR data of phomadecalin C (**3**) revealed the presence of an α,β-unsaturated ketone carbon at δ_C 199.3. Location of such a ketone carbonyl at C-3 would account for the downfield shifts in C-1/H-1 and C-9/H-9. Selective INEPT correlations of H-1 and H_3-15 to this ketone carbon confirmed its connection to C-2 and C-4. Since the remaining ^{1}H and ^{13}C NMR data closely matched those of phomadecalins A and B, the gross structure of phomadecalin C was assigned as shown in **3**.

FABMS and NMR data revealed that phomadecalin D (**4**) is the deacetylated analogue of phomadecalin B (**2**). The ^{1}H NMR spectrum of phomadecalin D (**4**) is essentially the same as that of phomadecalin B, except that the methyl singlet at δ_H 2.10 is absent, and the oxymethylene protons H_2-13 are shifted upfield from δ_H 4.80 and 4.70 to δ_H 4.17 and 4.04. Given the use of EtOAc in the extraction procedure, it is possible that phomadecalin B (**2**) is an artifact arising from selective, incidental acetylation of **4** during the isolation process. However, it was not possible to determine this with certainty by NMR analysis of the crude extract.

The relative stereochemistry of compounds **1**−**4** was presumed to be the same throughout the series because of the close similarities in the relevant ^{1}H and ^{13}C NMR shifts and *J*-values. The stereochemistry was proposed as shown by analysis of ^{1}H−^{1}H coupling constants and NOESY data for **1**−**4** and by comparison of the NMR data with those reported for phomenone and 8-β-hydroxyphomenone.[5,6] The large *trans*-diaxial-type coupling constant observed between H-3_{ax} and H-4 (13 Hz) in **1** indicated that H-4 must be in a pseudoaxial orientation with respect to the corresponding six-membered ring, placing H_3-15 in an equatorial position. The C-3 OH substituent in **2** and **4** was assigned a pseudoaxial orientation in each case due to the large coupling constant between H-3 and H-4 (ca. 10 Hz), as well as a NOESY correlation between H-3 and H_3-14. NOESY correlations of H-3_{ax} and H-6 to H_3-14 and H_3-15 and of H_3-14 to H_3-15 observed in all four compounds suggested

Table 3. ^{1}H and ^{13}C NMR Data for Phomapentenone A (**5**) in $CDCl_3$

pos.	δ_H (mult., *J* in Hz)	δ_C
1	0.94 (t, 7.8)	9.9
2	1.56 (m); 1.33 (m)	30.7
3	1.67 (m); 1.46 (ddd, 14, 9.6, 4.8)	36.5
4	3.80 (ddd, 9.6, 6.6, 3.0)	72.1
5	2.21 (dd, 6.6, 1.8)	56.7
6		210.4
7		140.7
8	7.30 (dq, 3.0, 1.2)	162.9
9	2.94 (m)	39.2
10	1.64 (m); 1.38 (ddd, 13, 9.6, 3.0)	41.7
11	3.64 (m)	71.4
12	1.50 (ddq, 12, 1.8, 6.6)	18.9
13	0.93 (t, 7.2)	9.9
14	1.73 (br s)	10.0

that H-6, H_3-14, and H_3-15 are all on the same face of the ring system, with CH_3-15 in an equatorial orientation and CH_3-14 in an axial orientation. The ^{1}H and ^{13}C NMR chemical shifts matched reasonably well with those of the corresponding signals reported for phomenone,[5] which possesses the same relative stereochemistry (originally established by X-ray crystallography). The limited differences observed are consistent with the variation in the functional groups at C-3.

The only relative configuration that could not be assigned by analysis of ^{1}H−^{1}H *J*-values and NOESY data was that of C-8, a stereocenter common to **1**−**4**. This assignment was made by spectral analogy to related known compounds. Phomadecalins A−D (**1**−**4**) are most closely related to the known compounds phomenone,[5] 8-*β*-hydroxyphomenone,[6] an analogue prepared from phomenone during structure−activity relationship studies, and a fungitoxic metabolite (13-desoxyphomenone) reported as a metabolite of *Hansfordia pulvinata*.[7] Of these, only the semisynthetic 8-*β*-hydroxyphomenone possesses an epoxycyclohexene ring with a substitution pattern identical to that of **1**−**4**. The H8−H9 coupling constant reported for this compound (2 Hz)[6] was consistent with the small *J*-value evident in the data for **1**−**4**. Assignment of the analogous orientation of H-8 in **1**−**4** as shown is also consistent with the absence of any NOESY correlations of H-8 with protons of the C11−C13 side chain.

A number of other fungal eremophilane sesquiterpenoids, such as phaseolinone,[8] a phytotoxin from *Macrophomina phaseolina*, and eremofortins A−E, isolated from *Penicillium roquefortii*[9,10] have also been reported. The differences between **1**−**4** and these known precedents involve the presence of the C1−C2 double bond, variations in positions of oxidation, and the identities of the functional groups present.

The molecular formula of the final compound obtained from *Phoma* sp. NRRL 25697 (phomapentenone A; **5**) was determined to be $C_{14}H_{24}O_3$ (three degrees of unsaturation) by FABMS and NMR data. Analysis of ^{1}H and ^{13}C NMR data (Table 3) showed that **5** is structurally and biogenetically quite different from **1**−**4**. These data revealed the presence of three methyl groups, four methylene units, four sp^3 methines (two of which are oxygenated), a trisubstituted olefin, and a ketone carbon. These signals, together with two exchangeable protons, accounted for the molecular formula and required phomapentenone A (**5**) to be monocyclic.

Analysis of COSY data led to identification of a single continuous spin-system incorporating all of the protons present in **5** except for one vinyl methyl group, and the connectivity of this unit was confirmed by selective INEPT correlations. Irradiation of vicinal protons H-4 and H-5 resulted in polarization transfer to the ketone carbon at δ_C 210.4 in each case, indicating that this ketone carbon (C-6) is connected to C-5. Correlations of the vinylic methyl signal (H_3-14) to C-6, as well as to the two olefinic carbons (C-7 and C-8), indicated that the olefin unit must be conjugated to the ketone carbon, with the methyl group located α to the ketone. Since the remaining linkages in the molecule were already established on the basis of COSY data, this resulted in assignment of a cyclopentenone ring. The chemical shifts for the ketone and olefinic carbons are fully consistent with such a structure.[11] The presence of two exchangeable protons can only be accounted for by placing hydroxy groups at the only oxygenated methine positions (C-4 and C-11). The relative stereochemistry at C-5 and C-9 was established by comparing the proton coupling constant between H-5 and H-9 with analogous couplings observed for other cyclopentenones.[12,13] In cyclopentene rings, a vicinal coupling constant of 5−6 Hz normally indicates a *cis* relationship, while a coupling constant of ca. 2 Hz suggests a *trans* relationship.[14−16] These observations have been extended to cyclopentenone rings, and a similar correlation has been observed.[12,13] Thus, in the case of **5**, the small coupling constant of 1.8 Hz is suggestive of a *trans* relationship between H-5 and H-9. The relative configurations at C-4 and C-11 were not determined.

Phomapentenone A (**5**) bears some resemblance to cyclopentenone-containing prostaglandins from various sources.[17,18] However, the fungal metabolites that are structurally most closely related to phomapentenone A include jasmonic acid derivatives from *Botryodiplodia theobromae*;[19] wasabienone B_0, a cyclopentenone derivative from *Phoma wasabiae*;[20] and terrein, originally isolated from *Aspergillus terreus*.[21] There are significant differences among these compounds, and wasabienone B_0 appears to be the closest relative from a biogenetic standpoint. Phomapentenone A (**5**) could be envisioned to arise from a heptaketide precursor by a pathway involving a ring contraction process somewhat analogous to the way in which wasabienone B_0 appears to arise from the polyketide-derived cyclohexadienone wasabidienone B_1.[20]

Compounds **1**−**5** were inactive against *Aspergillus flavus* and *Fusarium verticillioides* in disk assays at 250 μg/disk. However, **1**−**4** did exhibit activity in standard disk assays against *Bacillus subtilis* (ATCC 6051), causing zones of inhibition of 18, 10, 12, and 9 mm, respectively, at 200 μg/disk. Phomadecalins A (**1**), B (**2**), and D (**4**) also exhibited activity against *Staphylococcus aureus* (ATCC 29213), affording inhibitory zones of 10, 8, and 8 mm, respectively at the same level, but were inactive against *Candida albicans* (ATCC 90029) at this level.

Experimental Section

General Experimental Procedures. The optical rotations were measured on a DIP-1000 digital polarimeter (JASCO). ^{1}H NMR data were obtained at 300 MHz, and ^{13}C NMR data were obtained at 75 MHz (Bruker AC-300). COSY, HMBC, and NOESY data were recorded at 600 MHz (^{1}H-dimension; Bruker AMX-600). NMR data were recorded in $CDCl_3$ or $CDCl_3$−CD_3OD (4:1), and the chemical shifts were referenced to the residual solvent signals for $CDCl_3$ (δ_H 7.24/δ_C 77.0). Descriptions of MS, UV, and IR instrumentation have been published previously.[22]

Fungal Material. *Phoma* sp. (NRRL 25697) was isolated from a stroma of *Hypoxylon* sp. collected from a decaying log in Peoria, IL, by H. D. Thiers on May 7, 1996. The fungal strain was cultured on slants of potato dextrose agar (PDA) at 25 °C

for 14 days. Fermentation was carried out in duplicate 2.8 L Fernbach flasks each containing 200 g of rice. Spore inoculum was prepared by suspension in sterile distilled H_2O to give a final spore/cell suspension of 1×10^6/mL. Distilled H_2O (200 mL) was added to each flask, and the contents were soaked overnight before autoclaving at 15 1b/in.^{2} for 30 min. After cooling to room temperature, each flask was inoculated with 3.0 mL of the spore inoculum and incubated at 25 °C for 40 days.

Extraction and Isolation. The fermented rice substrate was first mechanically fragmented and then extracted with EtOAc (3 × 500 mL), and the combined EtOAc extracts were filtered and evaporated. The resulting crude extract (6.8 g) was fractionated by silica gel VLC using a CH_2Cl_2−MeOH gradient, collecting 200 mL fractions. The fraction that eluted with 98% CH_2Cl_2 (404 mg) was subjected to Sephadex LH-20 column chromatography using a hexane−CH_2Cl_2−acetone gradient solvent system. A subfraction (112 mg) that was eluted with CH_2Cl_2−acetone (4:1) was further separated by reversed-phase HPLC using CH_3CN−H_2O gradient elution (25%−30% CH_3-CN over 20 min, isocratic for 10 min, and then 25%−50% CH_3-CN over 10 min) on an Alltech HS Hyperprep 100 BDS 8-μm C_{18} column (250 × 10 mm) at 2.0 mL/min with UV detection at 254 nm to afford phomapentenone A (**5**; 2.3 mg; t_R 43 min). Another subfraction (65 mg) eluted with 4:1 CH_2Cl_2−acetone was also purified by reversed-phase HPLC using the same column as above (30%−35% CH_3CN over 25 min, 35%−45% CH_3CN over 25 min, isocratic for 5 min, and then 45%−100% over 5 min) to afford phomadecalins A (**1**; 5.0 mg; t_R 34 min), B (**2**; 3.0 mg; t_R 20 min), and C (**3**; 3.0 mg; t_R 13 min). A VLC fraction that was eluted with 95% CH_2Cl_2 (482 mg) was subjected to Sephadex LH-20 column chromatography using CH_2Cl_2−acetone (1:4) to afford a 45 mg subfraction, and further separation of this fraction by reversed-phase HPLC (15%−20% CH_3CN in H_2O over 50 min, isocratic for 10 min, and then 20%−50% CH_3CN over 10 min) afforded phomadecalin D (**4**; 7.5 mg; t_R 49 min).

Phomadecalin A (1): colorless oil; $[\alpha]_D$ +58° (*c* 0.050, 4:1 $CHCl_3$−MeOH); UV (MeOH) λ_{max} 226 (ϵ 2400), 278 (ϵ 1000); IR (4:1 $CHCl_3$−MeOH) ν_{max} 1617, 1462, 1385, 1224, 1025 cm^{-1}; ^{1}H NMR and ^{13}C NMR data, see Tables 1 and 2; selective INEPT data ($CDCl_3$; 300 MHz; H-# → C-#) H-1 → C-3, C-5, C-9, and C-10; H-2 → C-3, C-4, and C-10; H_2-3 → C-4; H-6 → C-5, C-7, C-10, and C-11; H-8 → C-9 and C-10; H-9 → C-1, C-5, and C-7; H_2-12 → C-7, C-11, and C-13; H_2-13 → C-7, C-11, and C-12; H_3-14 → C-4, C-5, C-6, and C-10; H_3-15 → C-3, C-4, and C-5; HRFABMS (3-NBA/NaI) obsd *m*/*z* 271.1302 (M + Na)$^+$, calcd for $C_{15}H_{20}O_3Na$, 271.1310.

Phomadecalin B (2): colorless oil; $[\alpha]_D$ +21° (*c* 0.083, 4:1 $CHCl_3$−MeOH); UV (MeOH) λ_{max} 224 (ϵ 3000), 272 (ϵ 1600); IR (4:1 $CHCl_3$−MeOH) ν_{max} 1620, 1456, 1381, 1224, 1025 cm^{-1}; ^{1}H NMR and ^{13}C NMR data, see Tables 1 and 2; selective INEPT data ($CDCl_3$; 300 MHz; H-# → C-#) H-1 → C-3, C-5, C-9, and C-10; H-6 → C-5, C-7, C-10, and C-11; H-9 → C-1, C-5, and C-7; H_2-12 → C-7, C-11, and C-13; H_3-14 → C-4, C-5, C-6, and C-10; H_3-15 → C-3, C-4, and C-5; FABMS (3-NBA/NaI) obsd *m*/*z* 329 ([M + Na]$^+$; rel int 100), 324 ([M + NH_4]$^+$; 28), 289 (13), 211 (73), 181 (20); HRFABMS (3-NBA/NaI) obsd *m*/*z* 329.1375 (M + Na)$^+$, calcd for $C_{17}H_{22}O_5Na$, 329.1365.

Phomadecalin C (3): colorless oil; $[\alpha]_D$ +210° (*c* 0.13, 4:1 $CHCl_3$−MeOH); UV (MeOH) λ_{max} 220 (ϵ 2600), 282 (ϵ 3000), 320 sh (600); IR (4:1 $CHCl_3$−MeOH) ν_{max} 2953, 2924, 1682, 1458, 1377, 1223 cm^{-1}; ^{1}H NMR and ^{13}C NMR data, see Tables 1 and 2; NOESY correlations $CDCl_3$ (H-# ↔ H-#); H-6 ↔ H_3-14 and H_3-15; H_3-14 ↔ H_3-15; selective INEPT data ($CDCl_3$; 300 MHz; H-# → C-#) H-1 → C-3, C-5, C-9, and C-10; H_3-15 → C-3, C-4, and C-5; FABMS (thioglycerol) obsd *m*/*z* 263 ([M + H]$^+$; rel int 23), 197 (15), 179 (7), 161 (11), 91 (100).

Phomadecalin D (4): pale yellow oil; $[\alpha]_D$ +13° (*c* 0.1, 4:1 $CHCl_3$−MeOH); UV (MeOH) λ_{max} 237 (ϵ 6600), 282 (ϵ 2200); IR (4:1 $CHCl_3$−MeOH) ν_{max} 2959, 2934, 1632, 1446, 1389, 1220, 1021 cm^{-1}; ^{1}H NMR and ^{13}C NMR data, see Tables 1 and 2; NOESY correlations (4:1 $CDCl_3$−CD_3OD; H-# ↔ H-#) H-6 ↔ H_3-14 and H_3-15; H-3 ↔ H_3-14; FABMS (3-nitrobenzyl alcohol/NaI) obsd *m*/*z* 287 ([M + Na]$^+$; rel int 3), 142 (14), 111 (8), 83 (35) 69 (68).

Phomapentenone A (5): colorless oil; $[\alpha]_D$ −90° (*c* 0.07, 4:1 $CHCl_3$−MeOH); UV (MeOH) λ_{max} 231 (ϵ 1800); IR (4:1 $CHCl_3$−MeOH) ν_{max} 2945, 2921, 1694, 1638, 1458, 1378, 1222 cm^{-1}; ^{1}H NMR and ^{13}C NMR data, see Table 3; selective INEPT data ($CDCl_3$; 300 MHz; H-# → C-#) H_3-1 → C-2 and C-3; H-4 → C-6 and C-9; H-5 → C-4 and C-6; H-8 → C-5, C-6, C-7, and C-9; H-9 → C-7, C-8, and C-10; H -11 → C-13; H_3-13 → C-11 and C-12; FABMS (thioglycerol) obsd *m*/*z* 241 ([M + H]$^+$; rel int 67), 223 (10), 205 (17), 151 (24), 109 (18), 91 (26); HRFABMS (thioglycerol) obsd *m*/*z* 241.1786, calcd for $C_{14}H_{25}O_3$, 241.1803.

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