Full Papers

Biologically Active Secondary Metabolites from Fungi. 12.[1] Oidiolactones A−F, Labdane Diterpene Derivatives Isolated from *Oidiodendron truncata*[§]

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Two known (**1** and **2**) and four new (**3**−**6**) diterpenes named oidiolactones A−F, respectively, and the antibiotic cladosporin were isolated from the fungus *Oidiodendron truncata*. The structure determination was mainly based on 1D and 2D NMR spectroscopy. The structures of compound **4**, displaying an equilibrium between open-chain and cyclized form, and of cladosporin were confirmed by X-ray analysis.

In connection with our program on the isolation of biologically active metabolites from fungi we have investigated the secondary metabolites of *Oidiodendron truncata* Barron. The fungus was isolated from an extreme location: the top of Enlang mountain (4000 m) in China. *Oidiodendron* belongs to the division of Deuteromycota and is an anamorphic genus of the teleomorphic genera *Myxotrichum* and *Byssoascus*. This paper describes the isolation and structure elucidation of the two known diterpenes PR 1388 (**1**)[2] and LL-Z 1271α (**2**),[3] four new diterpenes [3a,10b-dimethyl-6,6a-epoxy-1,2,3,3a,5a,7,10b,10c-octahydro-5,8-dioxaacephenanthrylene-4,9-dione (**3**), 7-hydroxy-3a,10b-dimethyl-6,6a-epoxy-1,2,3,3a,5a,7,10b,10c-octahydro-5,8-dioxaacephenanthrylene-4,9-dione (**4**), 10a-hydroxy-4b,8-dimethyl-3-oxo-3,4,4a,4b,5,6,7,8,8a,10a-decahydro-1*H*-2-oxaphenanthrene-8-carboxylic acid (**5**), and 4a-hydroxy-4b,8-dimethyl-3-oxo-3,4,4a,4b,5,6,7,8,8a,9-decahydro-1*H*-2-oxa-phenanthrene-8-carboxylic acid (**6**)] and of the known antibiotic, cladosporin. We propose to name these compounds (**1**−**6**) oidiolactones A−F, respectively, because diterpene PR 1388 (**1**) was also isolated from *Oidiodendron truncata*[1] and the oidiolactones are structurally related to the nagilactones,[4] inumakilactones,[5] and podolactones[6] (Figure 1).

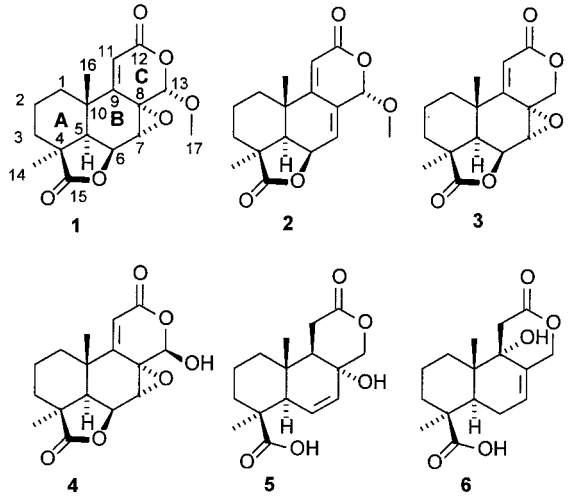

Figure 1. Structure of oidiolactones.

Results and Discussion

Compound **1** was obtained as colorless needles with a melting point of 231 °C. The molecular formula of $C_{17}H_{20}O_6$ and the spectral data (see Tables 1 and 2) confirmed the identity as PR 1388, which was first isolated by Rasmussen et al.[2] from *O. truncata*. The second compound, **2** (mp 222 °C), had spectral data similar to those of compound **1** and was identical with the antifungal agent LL-Z 1271α.[3] The structure was also confirmed by X-ray analysis (see Supporting Information).

Metabolite **3** was found in the same crude fraction as the diterpenes **1** and **2** but could be separated by repeated preparative TLC with a mixture of ethyl acetate−hexane (1:4) as the eluent. The molar weight and the molecular formula $C_{16}H_{18}O_5$ were determined by HRCIMS (*m*/*z* 290.115 ± 2 ppm). In analogy to compounds **1** and **2**, metabolite **3** showed the typical absorption of a γ-lactone in the IR spectrum (1778 cm^{-1}) and had almost identical ^1H and ^{13}C NMR resonances (see Tables 1 and 2). However, a remarkable difference in the ^1H and ^{13}C NMR spectra between **1** and **3** was the absence of the signal for the methoxy group in the spectra of compound **3**. Furthermore, a monooxygenated methylene group (δ 71.9) for C-13 was observed in the ^{13}C NMR spectrum of **3** instead of the two-fold oxygenated methine group (δ 99.9) of **1**. The corresponding proton signals (13-H) at δ 4.13 and 4.71 for the methylene group of compound **3** form an AB spin system and a geminal coupling constant of 12.4 Hz. From these data, and in agreement with the molecular formula, the structure proposed for compound **3** is as shown. The structure was further verified by the analysis of the HMBC spectrum. In this spectrum, the methylene group (H-13) displays ^2J and ^3J couplings to C-8, C-9, and C-12. The new diterpenoid **3** is assumed to have the same relative configuration as compound **1**, based on the similar coupling constants of the AMX spin system of H-5, H-6, and H-7

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Table 1. ^{1}H NMR Spectral Data for **1**−**6**[a]

H	1	2	3	4	5	6
1	1.44−1.80 (m, 2H)	1.51−1.90 (m, 2H)	1.40−1.76 (m, 2H)	1.39−1.74 (m, 2H)	1.05−1.22 (m, 2H)	1.33−1.44 (m, 1H), 1.80−1.97 (m, 1H)
2	1.44−1.80 (m, 2H)	1.51−1.90 (m, 2H)	1.40−1.76 (m, 2H)	1.39−1.74 (m, 2H)	1.45−1.49 (m, 1H), 1.44−1.57 (m, 1H)	1.55−1.63 (m, 1H), 1.87−2.04 (m, 1H)
3	1.44−1.80 (m, 1H), 2.15−2.28 (m, 1H)	1.51−1.90 (m, 1H), 2.27−2.42 (m, 1H)	1.40−1.76 (m, 1H), 2.15−2.28 (m, 1H)	1.39−1.74 (m, 1H), 2.10−2.20 (m, 1H)	1.81−1.88 (m, 1H), 2.18−2.22 (m, 1H)	1.01−1.20 (m, 1H), 2.14−2.24 (m, 1H)
4						
5	1.90 (d, 1H, J = 4.4 Hz)	1.96 (d, 1H, J = 4.8 Hz)	1.90 (d, 1H, J = 4.4 Hz)	1.80 (d, 1H, J = 4.4 Hz)	2.04 (dd, 1H)	2.13 (dd, 1H, J = 5.9 Hz, J = 11.3 Hz)
6	4.95 (dd, 1H, J = 4.4 Hz, J = 1.1 Hz)	5.06 (t, 1H, J = 4.6 Hz)	4.98 (dd, 1H, J = 4.4 Hz, J = 1.4 Hz)	4.90 (dd, 1H, J = 4.4 Hz, J = 1.1 Hz, 6-H)	6.65 (dd, 1H, J = 1.7 Hz, J = 10.4 Hz)	2.33−2.49 (m, 1H), 2.88−2.96 (m, 1H)
7	4.02 (d, 1H, J = 1.1 Hz)	6.60 (d, 1H, J = 4.6 Hz)	3.90 (d, 1H, J = 1.4 Hz)	3.92 (d, 1H, J = 1.1 Hz)	5.73 (dd, 1H, J = 3.0 Hz, J = 10.4 Hz)	5.89 (m, 1H)
8						
9					2.29 (d, 1H, J = 9.1 Hz)	
10						
11	6.04 (s, 1H)	5.80 (s, 1H)	6.04 (1H, s)	5.99 (s, 1H)	2.35 (d, 1H, J = 17.8 Hz), 2.95 (dd, 1H, J = 9.1 Hz, J = 17.8 Hz)	2.64 (d, 1H, J = 15.2 Hz), 2.80 (d, 1H, J = 15.2 Hz)
12						
13	5.46 (s, 1H)	5.78 (s, 1H)	4.13 (d, 1 H, J = 12.4 Hz), 4.71 (d, 1H, J = 12.4 Hz)	5.54 (brs, 1H)	3.46 (d, 1H, J = 11.4 Hz), 3.66 (d, 1H, J = 11.4 Hz)	4.79 (m, 1H, J = 12.6 Hz), 4.90 (m, 1H, J = 12.6 Hz)
14	1.29 (s, 3H)	1.37 (s, 3H)	1.30 (s, 3H)	1.23 (s, 3H)	1.30 (s, 3H)	1.28 (s, 3H)
15						
16	1.14 (s, 3H)	1.21 (s, 3H)	1.15 (s, 3H)	1.07 (s, 3H)	0.76 (s, 3H)	= 0.84 (s, 3H)
17	3.67 (s, 3H)	3.76 (s, 3H)				

[a] Assignment of protons and carbon atoms is based on labdane numbering in **1**.[2]

Table 2. ^{13}C NMR Spectral Data for **1**−**6**[a]

C	1	2	3	4	5	6
1	29.9 (t)	28.1 (t)	28.4 (t)	30.0 (t)	37.7 (t)	30.1 (t)
2	17.9 (t)	17.8 (t)	17.5 (t)	18.0 (t)	19.2 (t)	19.4 (t)
3	28.7 (t)	30.3 (t)	29.6 (t)	28.8 (t)	37.5 (t)	38.3 (t)
4	42.3 (s)	43.2 (s)	41.9 (s)	42.3 (s)	42.9 (s)	43.9 (s)
5	44.1 (d)	48.4 (d)	43.8 (d)	44.4 (d)	51.7 (d)	43.2 (d)
6	72.3 (d)	71.7 (d)	72.2 (d)	72.4 (d)	134.4 (d)	24.6 (t)
7	53.4 (d)	124.4 (d)	53.2 (d)	54.1 (d)	122.7 (d)	126.2 (d)
8	56.6 (s)	133.3 (s)	55.5 (s)	57.4 (s)	84.2 (s)	130.9 (s)
9	157.5 (s)	157.9 (s)	157.6 (s)	156.5 (s)	49.7 (d)	72.9 (s)
10	36.3 (s)	35.4 (s)	35.9 (s)	36.1 (s)	36.5 (s)	40.3 (s)
11	118.8 (d)	112.2 (d)	118.4 (d)	117.6 (d)	31.7 (t)	37.3 (t)
12	162.6 (s)	163.1 (s)	162.5 (s)	163.0 (s)	176.4 (s)	174.7 (s)
13	99.9 (d)	101.6 (d)	71.9 (t)		69.0 (t)	69.8 (t)
14	25.6 (q)	25.1 (q)	25.3 (q)	24.5 (q)	28.0 (q)	28.2 (q)
15	180.6 (s)	181.2 (s)	180.2 (s)	180.6 (s)	177.9 (s)	180.2 (s)
16	24.5 (q)	24.2 (q)	24.0 (q)	24.5 (q)	12.1 (q)	15.1 (q)
17	58.1 (q)	57.9 (q)				

[a] Assignment of protons and carbon atoms is based on labdane numbering in **1**.[2]

and the almost equal chemical shifts in the ^{1}H and ^{13}C NMR spectra. The natural product **3** is the first example of this class of lactone diterpenoid lacking a substituent at C-13.

Compound **4** was obtained from a crude polar fraction that also contained the compounds **5** and **6**. The mixture was separated by repeated preparative TLC on Si gel. The pure product **4** formed colorless needles (mp 241 °C). The molecular formula was deduced to be $C_{16}H_{18}O_6$ by DCI-HRMS. The IR spectrum showed the characteristic absorption band for a γ-lactone at 1788 cm^{-1} in addition to a broad band at 3336 cm^{-1}, a typical nonchelated hydroxyl group. The partial structure **A** (Figure 2) for $C_{15}H_{16}O_5R_1R_2$ could be deduced by analysis of the ^{1}H, ^{13}C, H−H COSY, C−H CORR, and HMBC spectra. Based on the difference in molecular weight between **1** (m/z 320 $[M]^+$) and **4** (m/z 306 $[M]^+$) and the characteristic OH resonance in the IR spectrum, the obvious structure **4** is as shown. However, one signal in the ^{13}C NMR for C-13 expected at ca. δ 100

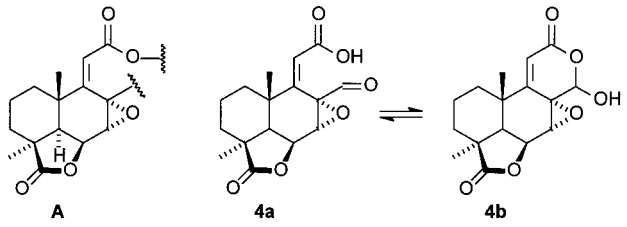

Figure 2. Partial structure **A** and equilibrium **4a**/**4b** of compound **4**.

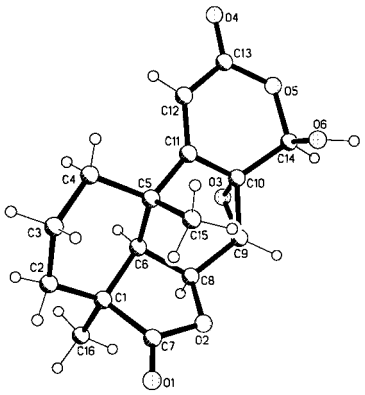

Figure 3. The crystalline structure of compound **4**.

was missing. Therefore, an equilibrium between an open-chain form **4a** and the cyclized hemiacetal **4b** is assumed (Figure 2).

An attempt to freeze the equilibrium at low temperature failed due to low solubility of the compound, but the assumption was supported by the occurrence of a small signal for an aldehyde proton in the ^{1}H NMR spectrum. In addition, a cross-peak not visible in the ^{13}C NMR at δ 97.2 was detected in the HMQC spectrum starting from the proton resonance at δ 5.54. Finally, the structure was confirmed by X-ray structure analysis (Figure 3) showing the β-configuration of 13-OH opposite to that of the methoxy group in **1** and the unusual hemiacetal-cyclic anhydride function of ring C. Compound **4** was not an artifact produced from **1** by hydrolysis, because the methyl

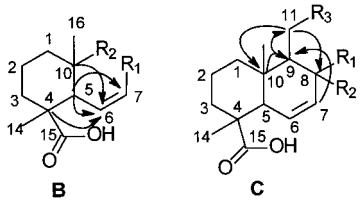

Figure 4. Partial structures **B** and **C** of compound **5**.

ether **1** was stable under the isolation and separation procedure as well as following acetic acid treatment for 14 days.

The natural product **5** (colorless prisms, mp 237 °C) has the molecular composition $C_{16}H_{22}O_5$ (HRCIMS) and shows intensive C=O absorption bands in the IR spectrum at 1719 and 1692 cm^{-1} and OH at 3400 cm^{-1}. The ^1H and ^{13}C NMR spectra of compounds **1** and **5** are similar in some chemical shifts and coupling patterns of ring A. The ^1H and H−H COSY spectra reveal ^3J and allylic ^4J couplings of 5-H in ring A with the olefinic protons 6-H and 7-H. Furthermore, cross signals in the HMBC spectrum between the quaternary C-4, C-10, and 6-H are detectable. These data and the absence of the characteristic IR absorption for a γ-lactone, together with the presence of a carboxy function, allow the construction of partial fragment **B** (Figure 4). Further analysis of the HMBC spectrum shows ^2J and ^3J correlations between C-7 and 9-H, and C-10 and 9-H. The proton 9-H couples with 11-H (H−H COSY) and 11-H correlates with the quaternary carbon atoms C-10 and C-8 (HMBC). The coupling of C-8 to 6-H leads to partial structure **C** (Figure 4).

Both 11-H and 9-H show a cross signal to the carbonyl group C-12 (HMBC), and a coupling is observable between C-9 and 13-H. Furthermore, a ^3J coupling between 13-H and C-7 is detectable, and the chemical shifts of C-8 and C-13 are characteristic for monooxygenated carbon atoms. The combination of these data leads to the construction of structure **5** (without stereochemical assignment) as shown. The relative configuration was determined by the analysis of the chemical shifts, coupling constants, and the NOE difference spectroscopy. Saturation of the proton resonances 14-H caused an increase of the intensity of 6-H (6%) and 5-H (3.5%), whereas the intensity of 16-H is unaffected. In addition, by irradiation of 16-H an increase in the intensity for 5-H was *not* observable. Accordingly, rings A and B must be trans fused in agreement with the analogues **1**−**4**. The cis connection of rings B and C is proven by the NOE of 16-H with the equatorially arranged proton 11-H. Furthermore, the strong lowfield shift of 11_a-H as compared to 11_e-H (0.6 ppm) is attributed to the interaction with the **axial** hydroxy group at C-8. This is in agreement with metabolites **1**−**4** and the entire labdene and labdadiene family, the presumable precursors of the natural products **1**−**6**.

Compound **6** has the same molecular formula and similar spectroscopic properties as **5**. However, the NMR resonances of ring B show remarkable differences in chemical shifts and coupling constants. Thus, the methine proton 5-H coupled with multiplets at δ 2.33−2.49 and δ 2.88−2.96 (H−H COSY), which are assigned by HMQC to the methylene group at δ 24.6 (C-6). In the H−H COSY spectrum, both multiplets show cross-peaks to the olefinic proton 7-H and to the protons at δ 4.79 and 4.90 (H-13). These protons form an ABMX spin system with a characteristic appearance, a large geminal coupling constant (J 12.6 Hz), an allylic ^4J coupling, and a homoallylic ^5J coupling. The proton 13-H correlates with the monooxygenated carbon atom C-9 (HMBC). Furthermore, this quaternary carbon atom coupled with 16-H and with the methylene group 11-H. The protons of 11-H form an AB spin system with a geminal coupling (15.2 Hz). In the HMBC spectrum both protons show a ^2J coupling to the lactone function at δ 174.7. These data lead to the construction of structure **6**. The relative configuration was again deduced by the analysis of the NOE difference spectra [H-14 and 6-H (6.5%), H-14 and 5-H (7.6%)] and coupling constants (11.3 Hz for 5-H and the axial 6-H) showing that rings A and B are trans linked. The cis connection of rings B and C are proved by the NOE of 16-H with the equatorial 11-H (7.2%). The highfield shift of 16-H (no deshielding from 9-OH) and the relative similarity of the chemical shifts of both protons 11-H support the trans axial arrangement of the methyl group at C-16 and 9-OH. It is plausible to assume a close biosynthetic connection among compounds **1**−**6**, which can be interconverted by simple chemical transformations such as allylic rearrangements and epoxidations.

Table 3. Biological Activity of the Pure Compounds[a]

	herbicidal			antifungal			antibacterial	
compound	Chl	Lep	Lem	Ust	Eur	Mm	Ec	Bm
1	2	4	3	2	1	1	0	1
2	3			4				1
4	1			1	1	1	0	0
5	1			1	1	0	0	0

[a] 10 mg/mL of compounds **1**, **2**, **4**, and **5** were tested for inhibitions of *Chlorella fusca* Shih Krauss (Chl), *Lemna minor* L. (Lem), *Lepidium sativum* L. (Lep), *Ustilago violacea* (Pers.) Roussel (Ust), *Eurotium repens* Corda (Eur), *Mycotypha microspora* Fenner (Mm), *Escherichia coli* (Mig.) Castell & Chambers (Ec) and *Bacillus megaterium* de Bary (Bm). Evaluation on a scale of 1−4: For the agar diffusion tests (Chl, Ust, Eur, Mm, Ec & Bm), a radius of inhibition of 1−10 mm = 1, 10−20 mm = 2, 20−30 mm = 3, 30−40 mm = 4. The plants were evaluated for growth inhibition and chlorotic symptoms: for Lep and Lem, inhibition in comparison to the controls 0 = < 40%, 1 = > 40%, 2 = > 60%, 3 = > 90%, 4 = 100%.

Cladosporin was isolated from the petroleum ether extract and purified by preparative TLC. The spectroscopic data and the X-ray analysis (see Supporting Information) proved the identity as cladosporin as previously isolated by Scott et al.[7] from *Aspergillus flavus* and *Aspergillus repens*. Cladosporin, which shows antimicrobial, insecticidal, and phytotoxic properties,[8] has not yet been reported as a secondary metabolite of the genus *Oidiodendron*.

Four of the isolated metabolites (**1**, **2**, **4**, **5**) were tested for herbicidal, antibacterial, and antifungal activities using established test systems (Table 3). Compounds **1** and **2** were strongly herbicidal, the remaining tested compounds exhibited moderate herbicidal activity. All of the substances exerted antifungal activities, in fact, compound **2** was strongly fungicidal against *Ustilago violacea*. Compounds **1** and **2** were also moderately antibacterial against the Gram-positive *Bacillus megaterium*.

Experimental Section

For general methods and instrumentation and microbiological methods and culture conditions see Krohn et al.[9,10] UV spectra were measured with a Perkin−Elmer Lambda 15 UV/vis spectrometer. Plates (20 × 20 cm) from Macherey−Nagel, Germany (1 mm Si gel) were used for preparative TLC. Compounds were detected on TLC by spraying with 8% aqueous H_2SO_4 and heating.

Isolation. The fungus *Oidiodendron truncata* Barron was incubated at 17 °C for 27 days in a biomalt (5% w/w; Vitaborn, Hameln, Germany) liquid culture. The cultures were homo-

genated using a Waring blender, and the homogenates were extracted successively once with petroleum ether and three times with EtOAc. The petroleum ether and the combined EtOAc extracts were dried (Na_2SO_4), filtered, and the filtrates evaporated at reduced pressure to afford a petroleum ether (0.2 g) and an EtOAc (2.3 g) crude extract. The EtOAc fraction was chromatographed on a Si gel column with a gradient of CH_2Cl_2−MeOH (0−5% of MeOH). By repeated TLC on Si gel with different mixtures of CH_2Cl_2−MeOH (98:2 for **1** and **3**, 97:3 for **4**, and 96:4 for **5** and **6**) and a mixture of EtOAc/hexane (1:4) (for **2**) compounds **1** (35 mg), **2** (10 mg), **3** (3 mg), **4** (15 mg), **5** (13 mg), and **6** (3 mg) were obtained.

Cladosporin (10 mg) was isolated from the petroleum ether fraction by TLC and crystallized from petroleum ether.

7-Methoxy-3a,10b-dimethyl-6,6a-epoxy-1,2,3,3a,5a,7,-10b,10c-octahydro-5,8-dioxaacephenanthrylene-4,9-dione, oidiolactone A (1): colorless needles (35 mg); mp 231 °C (CH_2Cl_2−cyclohexane); $[\alpha]^{20}_D$ +91° (*c* 0.98, MeOH); R_f 0.78 (CH_2Cl_2−MeOH 2%); IR (KBr) ν_{max} 3421, 1773, 1717, 1458 cm^{-1}; UV (CH_3OH) λ_{max} [nm] (ϵ) 225 (7900); CIMS *m*/*z* (%) 319 $[M - H]^-$ (25); HRCIMS 319.118 (calcd for $C_{17}H_{19}O_6$, 319.118); ^1H and ^{13}C data, see Tables 1 and 2.

7-Methoxy-3a,10b-dimethyl-1,2,3,3a,5a,7,10b,10c-octahydro-5,8-dioxaacephenanthrylene-4,9-dione, oidiolactone B (2): colorless crystals (10 mg); mp 222 °C (CH_2Cl_2−cyclohexane); $[\alpha]^{20}_D$ −206° (*c* 0.45, MeOH); R_f 0.74 (CH_2Cl_2−MeOH 2%); IR (KBr) ν_{max} 3398, 1765, 1735, 1720, 1459 cm^{-1}; UV (CH_3OH) λ_{max} (nm) (ϵ) 257 (10 500); ^1H and ^{13}C data, see Tables 1 and 2.

3a,10b-Dimethyl-6,6a-epoxy-1,2,3,3a,5a,7,10b,10c-octahydro-5,8-dioxaacephenanthrylene-4,9-dione, oidiolactone C (3): colorless crystals (3 mg); mp 223−224 °C (CH_2Cl_2−cyclohexane); $[\alpha]^{20}_D$ −13.2° (*c* 0.24, CH_2Cl_2); R_f 0.78 (CH_2Cl_2/MeOH 2%); IR (KBr) ν_{max} 1778, 1716, 1212, 1041, 951 cm^{-1}; UV (CH_3OH) λ_{max} (nm) (ϵ) 220 (6900), 253 (1000); EIMS *m*/*z* (%) 290 $[M]^+$ (2), 232 (25), 219 (70), 204 (80), 189 (50), 176 (45), 160 (100); HRCIMS 290.115 (calcd for $C_{16}H_{18}O_5$, 290.115); ^1H and ^{13}C data, see Tables 1 and 2.

7-Hydroxy-3a,10b-dimethyl-6,6a-epoxy-1,2,3,3a,5a,7,10b,10c-octahydro-5,8-dioxaacephenanthrylene-4,9-dione, oidiolactone D (4): colorless needles (15 mg); mp 241 °C (CH_3OH); $[\alpha]^{20}_D$ −34.1° (*c* 0.23; MeOH); R_f 0.62 (CH_2Cl_2−MeOH 4%); IR (KBr) ν_{max} 3336, 1788, 1696, 1089 cm^{-1}; UV (CH_3OH) λ_{max} (nm) (ϵ) 227 (7100); CIMS *m*/*z* (%) 324 $[M + NH_4]^+$ (100); HRDCIMS 305.10237 (calcd for $C_{16}H_{17}O_6$, 305.10251); ^1H and ^{13}C data, see Tables 1 and 2.

10a-Hydroxy-4b,8-dimethyl-3-oxo-3,4,4a,4b,5,6,7,8,8a,10a-decahydro-1*H*-2-oxaphenanthrene-8-carboxylic acid, oidiolactone, E (5): colorless prisms (13 mg); mp 237 °C (CH_3OH); $[\alpha]^{20}_D$ −38.5° (*c* 0.21, MeOH); R_f 0.31 (CH_2Cl_2−MeOH 4%); IR (KBr) ν_{max} 3400, 1719, 1692 cm^{-1}; UV (CH_3OH) λ_{max} (nm) (ϵ) 204 (2260), 230 sh; CIMS *m*/*z* (%) 294 $[M]^-$ (35), 276 $[M - H_2O]^+$ (100); HRCIMS 294.1504 (calcd for $C_{16}H_{22}O_5$, 294.1467); ^1H and ^{13}C data, see Tables 1 and 2.

4a-Hydroxy-4b,8-dimethyl-3-oxo-3,4,4a,4b,5,6,7,8,8a,9-decahydro-1*H*-2-oxaphenanthrene-8-carboxylic acid, oidiolactone F (6): colorless crystals (3 mg); mp 226 °C (CH_3OH); $[\alpha]^{20}_D$ −22.5° (*c* 0.08; MeOH); R_f 0.27 (CH_2Cl_2−MeOH 4%); IR (KBr) ν_{max} 3502, 3152, 1728, 1701 cm^{-1}; UV (CH_3OH) λ_{max} (nm) (ϵ) 204 (2300), 235 sh; DCIMS *m*/*z* (%): 293 $[M - H]^-$ (60), 292 (100); HRDCIMS 293.13890 (calcd for $C_{16}H_{21}O_5$, 293.13826); ^1H and ^{13}C data, see Tables 1 and 2.

Crystal Structure Determination of Compound 4.[11] $C_{16}H_{18}O_6$, M_r = 306.30, orthorhombic, space group $P2_1\,2_1\,2_1$, a = 829.6(2) pm, b = 1009.02 pm, c = 1720.9(3) pm, V = 1440.5(5) 10^6 pm^3, Z = 4, D_r = 1.412 mg/m^3, F (000) = 648, T = 210(2) K, Bruker AXS P4 diffractometer, graphite monochromator, λ (Mo Kα) = 71.073 pm, μ = 0.10 mm^{-1}, colorless crystal, size 0.55 × 0.50 × 0.30 mm, ω-scan, 1460 independent reflections θ range for data collection 2.73 to 25.07 °; limiting indices $0 \le h \le 9$, $0 \le k \le 12$, $0 \le l \le 20$, no absorption correction. Structure solved by direct methods,[12] full-matrix least-squares refinement based on F^2, 203 parameters,[11] all but H atoms refined anisotropically, H atoms located from difference Fourier maps and refined with riding model on idealized positions, refinement converged at $R1(F)$ = 0.0346, $wR2(F2$, all data) = 0.0860, S = 1.062, max(Δ/σ) < 0.001, min/max height in final ΔF map −0.126/0.173 e$Å^3$. Figure 2 shows the molecular structure.

Bioactivity Tests. Tests for antifungal, antibacterial, and herbicidal activities (with the exception of *Lemna minor*) were as previously described.[13] *L. minor* was cultivated prior to the test at 20 °C with a photoperiod of 16 h and light intensity of 210 μE/m^2 sec in the following medium: 0.4 g KNO_3, 5.04 g $CaCl_2$, 6.14 g $MgSO_4$, 0.2 g KH_2PO_4, 10 g sucrose, 1 mL of the trace element solution (34 mg $MnCl_2$, 50 mg H_3BO_3, 12 mg Na_2MoO_4, 5 mg $ZnSO_4$, 2.5 mg $CuSO_4$, 3.16 mg $CoCl_2$ in 100 distilled H_2O), 10 mL EDTA solution (50 mg Na_2EDTA, 20 mg $FeSO_4$ in 100 mL distilled H_2O), and 1000 mL distilled H_2O. To test for biological activity against *L. minor*, 10 mg of test substance was dissolved in 0.05 mL MeOH + 0.05 mL acetone and added to 10 mL test medium (the growth medium without sucrose) in Petri dishes (5 cm diameter) containing 15 test plants. Incubation was as above, and evaluation was performed after 1 and 6 days.

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Supporting Information Available: X-ray determination, ORTEP-plots and spectral data of oidiolactone (**2**) and of cladosporin. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(11) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 104518 (compound **4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].
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