33.21 (C-14), 26.73 (C-12), 25.35 (C-13); LRMS *m/e* (relative intensity) 383 (M^+, 3.52), 269 (2.47), 224 (1.5), 169 (2.12), 114 (3.7), 85 (8.9), 57 (100); HRMS calcd for $C_{14}H_{19}Cl_2NO_5S$ 383.03609, found 383.03542.

4-Thia-1-azabicyclo[3.2.0]heptane-2-carboxylic Acid, 6-Fluoro-3,3-dimethyl-7-oxo-, (2,2-Dimethyl-1-oxopropoxy)-methyl Ester, [2*S*(2α,5α,6β)]- (3e). To a solution of **3a** (69 mg, 0.17 mmol) and azobisisobutyronitrile (AIBN) (1 mg) in dry ether (5 mL) was added dropwise a solution of trineophyltin hydride (**5**) (104 mg, 0.2 mmol) in dry ether (2 mL) at room temperature. After the mixture was stirred for 5 h, the solvent was evaporated in vacuo, and the residue was chromatographed on silica gel column by using dichloromethane–hexane (60:40). The major fraction contained 38 mg (68%) of **3e** as an oil: IR (film) 1790 (β-lactam), 1770, and 1750 (ester) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (s, 9 H), 1.52 (s, 3 H), 1.66 (s, 3 H), 4.53 (s, 1 H, C-3H), 5.51 (t, 1 H, $J_{5,F}$ = 4 Hz, $J_{5,6}$ = 4 Hz, C-5H), 5.74 (dd, 1 H, $J_{6,F}$ = 55.8 Hz, $J_{5,6}$ = 4 Hz, C-6H), 5.77 and 5.88 (AB system, 2 H, J = 5.6 Hz, C-9H); ^{13}C NMR ($CDCl_3$) δ 176.59 (C-10), 169.02 (d, $^2J_{C,F}$ = 29.6 Hz, C-7), 166.12 (C-8), 91.77 (d, $^1J_{C,F}$ = 255 Hz, C-6), 79.84 (C-9), 70.52 (C-3), 66.57 (d, $^2J_{C,F}$ = 22 Hz, C-5), 64.14 (C-2), 38.67 (C-11), 31.55 (C-14), 26.73 (C-12), 26.55 (C-13); ^{19}F NMR ($CDCl_3$) δ −128.04 (dd, $^2J_{H,F}$ = 55.8 Hz, $^3J_{H,F}$ = 4 Hz); LRMS *m/e* (relative intensity) 333 (M^+, 6.84), 219 (2.06), 174 (2.22), 119 (2.66), 114 (2.5), 85 (8.72), 57 (100); HRMS calcd for $C_{14}H_{20}FNO_5S$ 333.1046, found 333.1061. The minor fraction was identified as the corresponding 6α-isomer **3d** (3%).

4-Thia-1-azabicyclo[3.2.0]heptane-2-carboxylic Acid, 6-Hydroxy-3,3-dimethyl-7-oxo-, (2,2-Dimethyl-1-oxopropoxy)-methyl Ester, [2*S*(2α,5α,6α)]- (3f). This compound was prepared according to a method described by Sheehan[18] for other penicillins: yield 75%; IR (film) 3466 (OH), 1780 (β-lactam and ester) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (s, 9 H), 1.47 (s, 3 H), 1.55 (s, 3 H), 4.32 (br s, 1 H, OH), 4.49 (s, 1 H, C-3H), 4.83 (d, 1 H, J = 1.6 Hz, C-6H), 5.26 (d, 1 H, J = 1.6 Hz, C-5H), 5.79 and 5.85 (AB system, 2 H, J = 5.6 Hz, C-9H); ^{13}C NMR ($CDCl_3$) δ 176.8 (C-10), 171.13 (C-7), 166.2 (C-8), 85.0 (C-6), 79.7 (C-9), 70.95 (C-5), 68.5 (C-3), 63.9 (C-2), 38.68 (C-11), 33.0 (C-14), 26.7 (C-12), 25.5 (C-13); LRMS *m/e* (relative intensity) 331 (M^+, 0.15), 274 (3.2), 244 (3), 217 (2.1), 160 (14.5), 144 (14), 85 (30), 57 (100).

4-Thia-1-azabicyclo[3.2.0]heptane-2-carboxylic Acid, 6-Fluoro-3,3-dimethyl-7-oxo-, (2,2-Dimethyl-1-oxopropoxy)-methyl Ester, [2*S*(2α,5α,6α)]- (3d).[11] **A: From 3f.** A solution of **3f** (215 mg, 0.65 mmol) in dry dichloromethane (2 mL) was added slowly to a solution of DAST (0.13 mL, 1.0 mmol) in dry dichloromethane (0.8 mL) at −23 °C under nitrogen. The reaction mixture was stirred for 6 h at room temperature, cooled to −10 °C, quenched with methanol (0.25 mL), and concentrated. Flash chromatography of the residue with chloroform–ether (95:05) as eluant yielded **3d** (164 mg, 75%) as white crystals, mp 62–64 °C. **B: From 2.** A 200-mg (0.59-mmol) sample of wet POM 6-diazopenicillanate (**2**) was dissolved in chloroform (4 mL) and cooled to 10 °C. DAST (0.147 mL, 1.173 mmol) in chloroform (1 mL) was added, and the mixture was stirred at this temperature for 15 h. After that the reaction mixture was cooled to −10 °C and methanol (0.25 mL) was added. Then the solvent was evaporated, and the crude product was purified by flash chromatography to give **3d** (195 mg, 65%).

4-Thia-1-azabicyclo[3.2.0]heptane-2-carboxylic Acid, 6-Fluoro-3,3-dimethyl-7-oxo-, (2,2-Dimethyl-1-oxopropoxy)-methyl Ester, 4,4-Dioxide, [2*S*(2α,5α,6α)]- (4a). To a solution of **3d** (133 mg, 0.4 mmol) in chloroform (10 mL) was added a solution of potassium permanganate (190 mg, 1.2 mmol) in water (10 mL). Then benzyltriethylammonium chloride (BTEAC, 10 mg, 0.04 mmol) was added, and the mixture was stirred vigorously at room temperature for 48 h. The mixture was filtered, the phases were separated, and the aqueous phase was extracted with chloroform (10 mL). The combined organic phase was washed with water containing hydrazine dihydrochloride (10 mL, 1 M) and brine (10 mL) and then was dried (Na_2SO_4). The solvent was removed to yield **4a** (116 mg, 80%) as a colorless oil: IR (film) 1810 (β-lactam), 1780 and 1755 (ester), 1330 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 s, 9 H), 1.43 (s, 3 H), 1.57 (s, 3 H), 4.45 (s, 1 H, C-3H), 4.67 (dd, 1 H, $J_{5,F}$ = 4.0 Hz, $J_{5,6}$ = 1.6 Hz, C-5H), 5.77 (dd, 1 H, $J_{6,F}$ = 53 Hz, $J_{5,6}$ = 1.6 Hz, C-6H), 5.75 and 5.96 (AB system, 2 H, J = 5.6 Hz, C-9H); ^{13}C NMR ($CDCl_3$) δ 176.6 (C-10), 164.7 (C-8), 164.6 (d, $^2J_{C,F}$ = 22 Hz, C-7), 91.3 (d, $^1J_{C,F}$ = 238 Hz, C-6), 80.5 (C-9), 67.4 (d, $^2J_{C,F}$ = 25 Hz, C-5), 63.1 (C-2), 62.6 (C-3), 38.7 (C-11), 26.7 (C-12), 19.7 (C-14), 18.1 (C-13); ^{19}F NMR ($CDCl_3$) δ −127.22 (dd, $^2J_{H,F}$ = 53 Hz, $^3J_{H,F}$ = 4.0 Hz); LRMS (CI, ammonia) *m/e* (rel intensity) 383 ($M^+ + NH_4$, 47), 357 (100), 325 (15), 264 (52), 232 (63), 116 (35).

4-Thia-1-azabicyclo[3.2.0]heptane-2-carboxylic Acid, 6-Fluoro-3,3-dimethyl-7-oxo-, (2,2-Dimethyl-1-oxopropoxy)-methyl Ester, 4,4-Dioxide, [2*S*(2α,5α,6β)]- (4b). Same procedure as **4a** using compound **3e** as the starting material. From 50 mg of **3e**, 43 mg (78%) of **4b** was obtained as a colorless oil: IR (film) 1820 (β-lactam), 1785 and 1765 (ester), 1340 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 9 H), 1.43 (s, 3 H), 1.60 (s, 3 H), 4.64 (s, 1 H, C-3H), 4.79 (dd, 1 H, $J_{5,F}$ = 3.2 Hz, $J_{5,6}$ = 4.0 Hz, C-5H), 5.88 (dd, 1 H, $J_{6,F}$ = 52 Hz, $J_{5,6}$ = 4.0 Hz, C-6H), 5.72 and 5.95 (AB system, 2 H, J = 5.6 Hz, C-9H); ^{13}C NMR ($CDCl_3$) δ 176.67 (C-10), 168.71 (d, $^2J_{C,F}$ = 24 Hz, C-7), 165.23 (C-8), 89.25 (d, $^1J_{C,F}$ = 240.2 Hz, C-6), 80.55 (C-9), 64.98 (d, $^2J_{C,F}$ = 22 Hz, C-5), 64.20 (C-2), 63.92 (C-3), 38.72 (C-11), 26.75 (C-12), 19.92 (C-14), 17.66 (C-13); ^{19}F NMR ($CDCl_3$) δ −121.02 (dd, $^2J_{H,F}$ = 52 Hz, $^3J_{H,F}$ = 3.2 Hz); LRMS (CI, ammonia) *m/e* (rel intensity) 383 ($M^+ + NH_4$, 100), 319 ($M^+ - SO_2 + NH_4$, 18), 232 (63), 83 (14).

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Supplementary Material Available: ^{13}C and ^1H NMR spectra for the new compounds (7 pages). Ordering information is given on any current masthead page.

Cytotoxic Hydroperoxylepidozenes from the Actinia *Anthopleura pacifica* Uchida

Guo-Chi Zheng,† Akio Ichikawa,† Midori O. Ishitsuka,† Takenori Kusumi,† Hiroshi Yamamoto,‡ and Hiroshi Kakisawa*,†

Department of Chemistry, The University of Tsukuba, Tsukuba, Ibaraki 305, Japan, and Faculty of Education, Ibaraki University, Bunkyo, Mito, Ibaraki 310, Japan

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Marine organisms are excellent sources of biologically active substances with unique chemical structures.[1] In the course of our studies on the pharmaceutically active compounds from marine animals, we have isolated several cytotoxic sesquiterpenes, including hydroperoxides **1**, **6**, and **8** from the acetone extract of the Okinawan actinia *Anthopleura pacifica* Uchida. We describe herein their structures (Chart I).

1,10-Epoxy-14-hydroperoxy-4-lepidozene (**1**), $[\alpha]_D$ −143° (*c* 0.12, $CHCl_3$), an unstable colorless oil, exhibits a molecular peak at *m/z* 252, which corresponds to $C_{15}H_{24}O_3$, in the mass spectrum. The IR spectrum (film) shows the absorptions due to the hydroxy group at 3400 cm^{-1}. The ^1H NMR spectrum (500 MHz, C_6D_6) reveals an extremely shielded signal at δ 0.01 (1 H, ddd), which is apparently ascribable to a proton on a cyclopropane ring. The ^1H–^1H COSY-45[2] and ^1H–^{13}C COSY spectra established the vicinal relation of the proton and another shielded proton at δ 1.00. The 1D ^1H NMR spectrum shows that the

† The University of Tsukuba.
‡ Ibaraki University.

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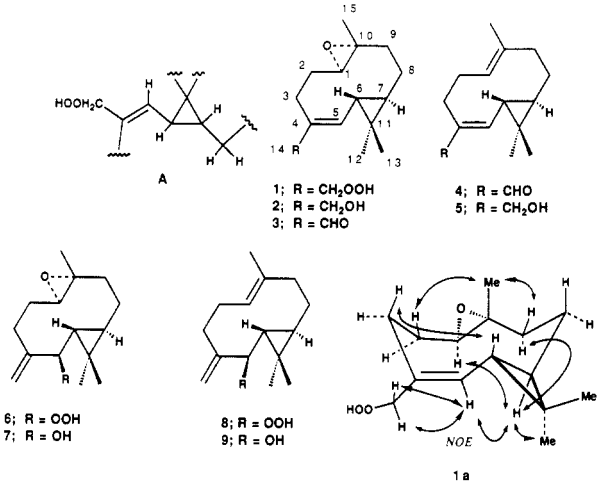
Chart I



cyclopropane protons were mutually coupled with $J = 5.5$ Hz, suggesting the trans relationship of them.[3] The signal at δ 1.00 is further coupled with the olefinic proton at δ 5.37 (d, $J = 9$ Hz), and this proton is long-range coupled with the oxymethylene protons [δ 4.28 (d, $J = 11.5$ Hz) and 4.42 (d, $J = 11.5$ Hz)]. The oxymethylene carbon shows a signal at δ 82.2 (t) in the ^{13}C NMR spectrum. The chemical shift is rather low for ordinary allylic hydroxymethylene carbons and was reminiscent of the hydroperoxymethylene carbon.[4] The mass fragments at m/z 236 ($M^+ - O$), 234 ($M^+ - H_2O$), and 218 ($M+ - H_2O_2$) support the presence of a hydroperoxy group.[4,5] Also the positive iodine–starch test as well as the appearance of the ^1H NMR signal at δ 7.40 (OO*H*) verified the presence of the hydroperoxide[4]. Appearance of NOE cross peaks between the olefinic proton (δ 5.37) and the hydroperoxymethylene protons in the NOESY spectrum confirmed the *E* configuration of the olefin bond. The cyclopropane methine proton at δ 0.01 appears as a ddd ($J = 11$, 5.5, 2.5 Hz), which is correlated to the signal at δ 0.91. The homo- and heteronuclear COSY spectra indicate the geminal relationship of this with the signal at δ 1.73 [^{13}C; δ 25.6 (t)]. On the basis of these spectral data, the partial structure A was deduced. Besides the moieties described above, the NMR spectra of **1** suggests the presence of a *gem*-dimethyl [^1H, δ 0.99 (3 H, s), 1.00 (3 H, s); ^{13}C, δ 22.0 (q), 22.6 (q), 21.4 (s)], a methyl-substituted oxirane [^1H; δ 2.97 (1 H, dd), 1.20 (3 H, s); ^{13}C; δ 59.2 (s), 62.5 (d), 16.3 (s)], and three methylene groups [^{13}C; δ 25.9, 29.1, 41.0 (all t)]. Detailed analysis of the ^1H–^1H COSY spectrum led to the planer structure **1**, the stereochemistry of which was unambiguously determined as in **1a** by means of the phase-sensitive NOESY spectrum. To our knowledge, **1** is the first natural product possessing an allylic hydroperoxymethylene moiety.

The structure **1** was further confirmed by reduction of the hydroperoxy moiety with triphenylphosphine, affording the alcohol **2**. The resulting hydroxymethylene carbon (C-14) exhibits a ^{13}C NMR signal at δ 67.5 (t).

Further separation resulted in the isolation of the aldehyde **3**, IR ($CHCl_3$) 2930, 1670, 1627 cm^{-1}, which was closely related with **1**. This aldehyde has been prepared by a peracid epoxidation of (−)-lepidozenal (**4**).[6] In fact, we were able to isolate (−)-**4** [$[\alpha]_D$ −236° (*c* 0.3, $CHCl_3$)] together with (−)-**5** [$[a]_D$ −109° (*c* 0.18, $CHCl_3$)]. It is worth noting that **4** and **5** from the marine actinia have the same chiroptical properties as (−)-lepidozenal (**4**) [lit.[6] $[\alpha]_D$ −169° (*c* 1.11, $CHCl_3$)] and (−)-lepidozenol (**5**) [lit.[6] $[\alpha]_D$ −104° (*c* 1.75, $CHCl_3$)], which occur in liverwort.[6] Detailed analysis of the NOESY spectrum of **3** revealed that this compound possesses a conformation very similar to that of **1a**.

1,10-Epoxy-5-hydroperoxy-4(14)-lepidozene (**6**), $[\alpha]_D$ −68.1° (*c* 0.07, EtOH), was obtained as a minor component. Although this compound was extremely unstable, the structure could be deduced by quick measurement of the ^1H–^1H COSY spectrum. Interestingly, on standing a solution of **6** in C_6D_6 at 5 °C for 48 h gave a mixture of **6** and **1** (1:1). However, **1** was not changed to **6** under these conditions. A similar type of migration of an allylic hydroperoxy group has been recently reported.[7]

The spectral properties of 1,10-epoxy-4(14)-lepidozen-5-ol (**7**), $[\alpha]_D$ −76° (*c* 0.09, $CHCl_3$), are quite similar to those of **6**, except for the signal of C–5 at δ 78.3 (d) [**6**; δ 91.4 (d)] and the absence of the ^1H signal due to OOH (δ 7.37) of **6**. Possibly because of conformational flittering, several carbon signals become very broad and only nine signals were observed in the ^{13}C NMR spectrum of **7**.

An analogous pair of a hydroperoxide and an alcohol were obtained from the less polar fraction: Lepidoza-1(10),4(14)-dien-5-ol (**9**), $[\alpha]_D$ −35.0° (*c* 0.24, EtOH), represents the NMR spectral properties quite similar to those of 5-hydroperoxylepidoza-1(10),4(14)-diene (**8**), $[\alpha]_D$ −20.4° (*c* 0.23, EtOH), except that the chemical shift (δ 79.9) of the oxygen-bearing carbon (C-5) is shifted upfield relative to that (δ 92.7) of **8**. Eventually these two compounds were chemically correlated to each other by reduction of **8** (triphenylphosphine) to give **9**.

The present sesquiterpenoids exhibit the following cytotoxicity against murine melanoma cells (IC_{50}, $\mu g/mL$): **1**, 0.7; **4**, 3.8; **5**, 4.5; **6**, 2.3; **8**, 0.9; **9**, 4.2.

Experimental Section

General Instrumentation. The IR spectra were recorded on a Hitachi 215 spectrophotometer. ^1H and ^{13}C NMR spectra were taken on a Bruker AM-500 spectrometer. GC-MS spectra were measured on a Hitachi RMU-6M spectrometer, using a glass column (1% OV-1; 0.5 cm × 100 cm). Optical rotations were recorded on a JASCO DIP-181 polarimeter using a 10-cm microcell.

Materials. *Anthopleura pacifica* Uchida (2 kg) was collected in June 1988 at the Henoko beach in Okinawa Island. A voucher specimen is preserved at the Experimental Fishery Station at Okinawa (Itoman). The actinia was soaked in acetone immediately after collection and the mixture was allowed to stand for 1 week. The acetone extract was concentrated, and the residue was successively washed with hexane, dichloromethane, and ethyl acetate. The hexane extract was concentrated to give a dark brown residue (27.6 g), and this material (12.9 g) was chromatographed on silica gel (Merck, Kieselgel 60; hexane–EtOAc) to give 11 fractions (I, II, ... XI). The ^1H NMR spectrum of the fourth fraction (fr. IV) (1.45 g) exhibited a group of signals at around 0.0 ppm. Further

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separation of this fraction by flash chromatography (Wakogel, C-300; CH_2Cl_2) afforded 5 fractions, two of which, designated fr. A (540 mg) and fr. B (214 mg), showed the cyclopropane signals in the ^1H NMR spectrum. Repeated separation of fr. A by preparative TLC (Merck, Kieselgel 60, GF_{254}) afforded **8** (5 mg), **9** (3 mg), and **5** (3 mg). Separation of fr. B produced **4** (3 mg) and **9** (8 mg). Similarly, **1** (7 mg) and **6** (3 mg) were obtained from fr. VII (0.5 g), **3** (2 mg) from fr. V (1.2 g), and **7** (2 mg) from fr. IX (0.5 g).

1,10-Epoxy-14-hydroperoxy-4-lepidozene (1). High-resolution MS: *m/e* 252.1724 (M^+, $C_{15}H_{24}O_3$). ^1H NMR spectrum (500 MHz, C_6D_6): δ 0.01 (1 H, ddd, *J* = 11, 5.5, 2.5 Hz, H-7), 0.91 (1 H, m, H-8), 0.99 (3 H, s, H-13), 1.00 (3 H, s, H-12), 1.00 (1 H, overlapping; H-6), 1.16 (1 H, td, *J* = 13, 2.5 Hz; H-9), 1.20 (3 H, s, H-15), 1.45 (1 H, m, H-2), 1.73 (1 H, ddt, *J* = 14, 5, 2.5 Hz, H-8), 2.08 (1 H, dt, *J* = 13, 4 Hz, H-3), 2.12 (1 H, ddd, *J* = 13, 5, 2.5 Hz, H-9), 2.34 (1 H, tt, *J* = 13, 4 Hz, H-2), 2.43 (1 H, td, *J* = 13, 4 Hz, H-3), 2.97 (1 H, dd, *J* = 10, 4 Hz, H-1), 4.28 (1 H, d, *J* = 11.5 Hz, H-14), 4.42 (1 H, d, *J* = 11.5 Hz, H-14), 5.37 (1 H, d, *J* = 9 Hz, H-5), 7.40 (1 H, s, OOH). ^{13}C NMR spectrum (125 MHz, C_6D_6): δ 16.3 (q, C-15), 21.4 (s, C-11), 22.0 (q, c-13), 22.6 (q, C-12), 25.6 (t, C-8), 25.9 (t, C-3), 29.1 (t, C-2), 31.6 (d, C-6), 34.7 (d, C-7), 41.0 (t, C-9), (s, C-10), 62.5 (d, C-1), 82.2 (t, C-14), 132.6 (d, C-5), 133.7 (s, C-4).

1,10-Epoxylepidozenol (2). ^1H NMR spectrum (500 MHz, C_6C_6): δ 0.05 (1 H, ddd, *J* = 9, 4, 2 Hz, H-7), 1.00 (1 H, tdd, *J* = 13, 9, 3 Hz, H-8), 1.05 (1 H, dd, *J* = 8, 4 Hz, H-6), 1.06 (3 H, s, H-12/13), 1.12 (3 H, s, H-13/12), 1.24 (1 H, td, *J* = 13, 3 Hz, H-9), 1.27 (3 H, s, H-15), 1.46 (1 H, ddt, *J* = 13, 9, 4 Hz, H-2), 1.82 (1 H, bd, *J* = 13 Hz, H-8), 2.05 (1 H, dt, *J* = 13, 4 Hz, H-3), 2.18 (1 H, ddd, *J* = 13, 6, 3 Hz, H-9), 2.30 (1 H, tt, *J* = 13, 4 Hz, H-20), 2.47 (1 H, td, *J* = 13, 4 Hz, H-3), 2.96 (1 H, dd, *J* = 9, 4 Hz, H-1), 3.87 (1 H, d, *J* = 9 Hz, H-14), 3.96 (1H, d, *J* = 9 Hz, H-14), 5.36 (1 H d, *J* = 8 Hz, H-5). ^{13}C NMR spectrum [125 NHz (DEPT), C_6D_6; only the region 0–100 ppm was measured]: δ 16.3 (q, C-15), 22.1 (q, C-12/13), 22.8 (q, C-13/12), 25.3 (t, C-8/3), 25.9 (t, C-3/8), 29.2 (t, C-2), 31.6 (d, C-6), 34.6 (d, C-7), 41.2 (t, C-9), 62.4 (d, C-1), 67.5 (t, C-14).

1,10-Epoxylepidozenal (3). ^1H NMR spectrum (500 MHz, $CDCl_3$): δ 0.69 (1 H, ddd, *J* = 11.5, 5, 3 Hz, H-7), 1.10 (1 H, td, *J* = 12, 3 Hz, H-9), 1.20 (3 H, s, H-15), 1.24 (3 H, s, H-12/13), 1.29 (1 H, m, H-8), 1.36 (3 H, s, H-13/12), 1.44 (1 H, dd, *J* = 10, 5 Hz, H-6), 1.44 (1 H, m, H-2), 2.10 (1 H, ddt, *J* = 15, 5, 3 Hz, H-8), 2.19 (1 H, tt, *J* = 13, 4 Hz, H-2), 2.21 (1 H, m, H-9), 2.31 (1 H, td, *J* = 13, 5 Hz, H-3), 2.68 (1 H, dd, *J* = 10, 4 Hz, H-1), 2.72 (1 H, ddd, *J* = 13, 5, 4 Hz, H-3), 6.41 (1 H, d, *J* = 10 Hz, H-5), 9.37 (1 H, s, H–14).

(−)-Lepidozenal (4). ^1H NMR spectrum (500 MHz, C_6D_6): δ 0.13 (1 H, ddd, *J* = 11.5, 5, 3 Hz), 0.72 (1 H, tdd, *J* = 14, 12, 3 Hz), 0.90 (3 H, s), 0.92 (1 H, dd, *J* = 10, 5 Hz), 0.95 (3 H, s), 1.42 (3 H bs), 1,65 (1 H, dq, *J* = 14, 3 Hz), 1.86 (1 H, td, *J* = 13, 3 Hz), 2.01 (1 H, td, *J* = 13, 5 Hz), 2.08 (1 H, dt, *J* = 13, 4 Hz), 2.18 (1 H, tdd, *J* = 13, 7, 4 Hz), 2.43 (1 H, m), 2.94 (1 H, ddd, *J* = 12, 4, 3 Hz), 5.00 (1 H, bt, *J* = 7 Hz), 5.96 (1 H, d, *J* = 10 Hz), 9.38 (1 H, d, *J* = 1 Hz).

(−)-Lepidozenol (5). ^1H NMR spectrum (500 MHz, $CDCl_3$): δ 0.11 (1H, ddd, *J* = 11.5, 5, 3 Hz), 0.76 (1 H, dd, *J* = 9, 5 Hz), 0.89 (1 H, tdd, *J* = 13, 11.5, 3 Hz), 1.01 (3 H, s), 1.09 (3 H, s), 1.62 (3 H, d, *J* = 1.5 Hz), 1.87 (1 H, dq, *J* = 13, 3 Hz), 1.99 (2 H, m), 2.08 (1 H, m), 2.21 (1 H, dt, *J* = 13, 3 Hz), 2.40 (2 H, m), 4.01 (1 H, d, *J* = 12 Hz), 4.11 (1 H, d, *J* = 12 Hz), 5.16 (1 H, bt, *J* = 7.5 Hz), 5.30 (1 H, d, *J* = 9 Hz). ^{13}C NMR spectrum (125 MHz, $CDCl_3$) (assignments; see above): δ 15.5 (q, C-15), 16.6 (s, C-11), 21.8 (q, C-12/13), 22.4 (q, C-13/12), 24.6 (t, C-2/3/8), 26.9 (t, C-3/2/8), 27.1 (t, C-8/3/2), 31.7 (d, C-7), 34.3 (d, C-6), 40.4 (t, C-9), 68.2 (t, C-14), 125.9 (d, C-1/5), 128.5 (d, C-5/1), 133.3 (s, C-4/10), 136.8 (s, C-10/4).

1,10-Epoxy-5-hydroperoxy-4(14)-lepidozene (6). High-resolution MS: *m/e* 252.1734 (M^+, $C_{15}H_{24}O_3$). ^1H NMR spectrum (500 MHz, C_6D_6): δ 0.08 (1 H, bdd, *J* = 11, 5 Hz, H-7), 0.34 (1 H, dd, *J* = 10, 5 Hz, H-6), 0.76 (1 H, ddd, *J* = 14, 11, 3 Hz, H-8), 1.04 (3 H, S, H-12/13), 1.13 (3 H, s, H-13/12), 1.20 (3 H, s, H-15), 2.78 (1 H, dd, *J* = 10, 3.5 Hz, H-1), 3.90 (1 H, d, *J* = 10 Hz, H-5), 5.00 (1 H, s, H-14), 5.22 (1 H, s, H-14), 7.37 (1 H, s, OOH). (Satisfactory ^{13}C NMR spectrum was not obtained because of decomposition during accumulation.)

1,10-Epoxy-4(14)-lepidozen-5-ol (7). ^1H NMR spectrum (500 MHz, $CDCl_3$): δ 0.20 (1 H, bdd, *J* = 10, 5.5 Hz, H-7), 0.56 (1 H dd, *J* = 9.5, 5.5 Hz, H-6), 1.02 (2 H, m, H-8), 1.11 (3 H, s, H-12/13), 1.15 (3 H, s, H-13/12), 1.22 (3 H, s, H-15), 1.45 (1 H, ddd, *J* = 13.5, 6, 3.5 Hz, H-2), 1.98 (1 H, m, H-9), 2.13 (1 H, m, H-9), 2.20 (1 H, m, H-3), 2.32 (1 H, tt, *J* = 13.5, 3.5 Hz, H-2), 2.38 (1 H, m, H-3), 2.89 (1 H, dd, *J* = 10.5, 3.5 Hz, H-1), 3.70 (1 H, d, *J* = 9.5 Hz, H-5), 5.10 (1 H, s, H-14), 5.22 (1 H, s, H-14). ^{13}C NMR spectrum [125 MHz, $CDCl_3$] (only nine signals were observed.): δ 16.0, 22.0, 22.0, 25.6, 27.8, 28.6, 39.6, 78.3, 144.3.

5-Hydroperoxylepidoza-1(10),4(14)-diene (8). High-resolution MS: *m/e* 236.1780 (M^+, $C_{15}H_{24}O_2$). ^1H NMR spectrum (500 MHz, $CDCl_3$): δ 0.04 (1 H, dd, *J* = 10, 5 Hz, H-6), 0.28 (1 H, ddd, *J* = 11, 5, 2 Hz, H-7), 0.95 (1 H, m, H-8), 1.00 (3 H, s, H-12/13), 1.15 (3 H, s, H-13/12), 1.53 (3 H, bs, H-15), 1.88 (1 H, m, H-8), 1.92 (1 H, m, H-3), 1.98 (1 H, td, *J* = 13, 4.5 Hz, H-9), 2.12 (1 H, m, H-2), 2.18 (1 H, bdt, *J* = 13, 4 Hz, H-9), 2.39 (1 H, dtd, *J* = 13, 11, 4 Hz, H-2), 2.52 (1 H, m, H-3), 3.85 (1 H, d, *J* = 10 Hz, H-5), 5.18 (1 H, ddq, *J* = 11, 5.5, 1 Hz, H-1), 5.26 (1 H, s, H-14), 5.32 (1 H, s, H-14), 7.70 (1 H, s, OOH); ^{13}C NMR spectrum (125 MHz, C_6D_6) (only 12 signals were observed): δ 18.5, 21.9, 22.8, 26.2, 30.0, 31.1, 34.9, 39.8, 92.7, 114.0, 126.1, 137.3.

Lepidoza-1(10),4(14)-dien-5-ol (9). High-resolution MS: *m/e* 220.1847 (M^+, $C_{15}H_{24}O$). ^1H NMR spectrum (500 MHz, C_6D_6): δ 0.06 (1 H, ddd, *J* = 11, 5.5, 2.5 Hz, H-7), 0.33 (1 H, dd, *J* = 10, 5.5 Hz, H-6), 0.95 (1 H, m, H-8), 1.09 (3 H, s, H-12/13), 1.20 (3 H, s, H-13/12), 1.52 (3 H, s, H-15), 1.78 (1 H, dtd, *J* = 14, 4, 2.5 Hz, H-8), 1.93 (1 H, m, H-3), 1.96 (1 H, td, *J* = 13, 4 Hz, H-9), 2.10 (1 H, m, H-3), 2.17 (1 H, dt, *J* = 13, 4 Hz, H-9), 2.37 (2 H, m, H-2), 3.49 (1 H, d, *J* = 10 Hz, H-5), 4.97 (1 H, s, H-14), 5.22 (1 H, s, H-14), 5.23 (1 H, bt, *J* = 8 Hz, H-1). ^{13}C NMR spectrum (125 MHz, $CDCl_3$) (one signal is missing): δ 16.1, 17.8, 22.1, 22.2, 26.1, 29.1, 29.8, 37.7, 39.5, 79.9, 114.3, 124.9, 125.9, 133.6.

Reduction of the Hydroperoxides 1 and 8 with Triphenylphosphine. A solution of **1** (700 μg) and triphenylphosphine (1 mg) in benzene (1 mL) was allowed to stand at room temperature for 2 h. TLC (Merck, Keiselgel GF 254; CH_2Cl_2) of the product showed the spots corresponding to triphenylphosphine, triphenylphosphine oxide, and a reduction product. Separation with column chromatography (Merck, Kieselgel 60) afforded **2** (500 μg), which was identified by comparison of its R_f in TLC and ^1H NMR spectrum with those of authentic sample. Reduction of **8** (500 μg) was carried out in the same manner, yielding **9** (300 μg).

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Light-Induced, Iodine-Catalyzed Aerobic Oxidation of Unsaturated Tertiary Amines

Anthony R. Gangloff, Thomas M. Judge, and Paul Helquist*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

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Numerous methods have been reported for the oxidation of amines through use of chemical, electrochemical, microbiological, and photochemical procedures. Among the nonphotochemical methods[1,2] are reactions employing dichromate, lead tetraacetate, manganese dioxide, per-

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