Parectadial, a Monoterpenoid from the Defensive Spray of *Parectatosoma mocquerysi*

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The defensive secretion of *Parectatosoma mocquerysi*, a walkingstick insect from Madagascar, was determined to contain glucose, water, and a new monoterpene, parectadial, (4*S*)-(3-oxoprop-1-en-2-yl)cyclohex-1-enecarbaldehyde. Here, we describe the elucidation of parectadial's molecular structure and absolute configuration via microsample NMR technology, GC-MS, CD, chiral GC-FID, and synthesis from enantiomerically pure (*S*)- and (*R*)-perillaldehyde. This work demonstrates the value of walkingstick insects as sources of new bioactive compounds and provides an analytical framework for identifying such substances.

Insects as a group employ a diverse repertoire of chemical compounds for the purpose of warding off predators.[1] Walkingstick insects (order Phasmatodea) appear to be no exception. Of the hundreds of species of phasmids that have been identified worldwide, many are known to produce a defensive secretion, usually from a thoracic gland just behind the head. However, the chemical composition of only a few of their defensive secretions have been characterized,[2−9] and most contain at least one monoterpenoid. Here we report a new monoterpene dialdehyde, (4*S*)-(3-oxoprop-1-en-2-yl)cyclohex-1-enecarbaldehyde, which is the major component in the defensive secretion of *Parectatosoma mocquerysi* Finot 1897, a walkingstick insect native to Madagascar[10,11] (Figure 1). We call this new compound parectadial (**1**) and show how it can be synthesized from (4*S*)- and (4*R*)-perillaldehydes (**3** and **4**). Parectadial has one stereocenter, and only the *S* isomer (**1**) has been isolated from the insect. The synthesis of parectadial also produces a tertiary alcohol, 4-hydroxy-4(prop-1-en-2-yl)cyclohex-1-enecarbaldehyde (**5**), which we are calling 4-perillyl alcohol since it has not been previously characterized. This study provides the analytical framework for rapidly characterizing novel compounds from walkingstick insects that can be subsequently screened for biological activity.

Results and Discussion

For an initial structure analysis using GC-CIMS, 1 μL of crude *P. mocquerysi* defensive spray was dissolved in 500 μL of methyl-*tert* butyl ether (MTBE) to yield an amenable solution containing a single compound with *m*/*z* 165 $[M + H]^+$ (Supporting Information S1). On the basis of GC-EIMS spectra and monoterpenoid structures from other phasmid defensive secretions,[2,3,5−8] we concluded that the active component of *P. mocquerysi* spray had the molecular formula $C_{10}H_{12}O_2$ (Supporting Information S1). Further investigation of the molecular structure was primarily by NMR.

One-dimensional (1D) ^{1}H NMR spectra were acquired of the crude defensive spray both dissolved in D_2O and extracted with benzene-d_6 (see Figure S2 in Supporting Information). The D_2O spectrum showed only 12 resonances (each integrating to one), a set of peaks readily attributable to glucose, and a few minor low-frequency peaks. The benzene spectrum contained only 12 proton resonances (each integrating to one) besides the solvent signal. Of these, there were two resonances in the aldehyde region (δ_H 9.15 and 9.23) and three in the vinyl region (δ_H 5.18, 5.41, and 5.89). The less shielded vinyl resonance (δ_H 5.89) showed a strong COSY correlation to one proton (δ_H 2.07) (Supporting Information Figure S3), medium COSY to another (δ_H 1.49), and weak COSY correlations to two others (δ_H 2.32 and 1.96). From the HMQC it was clear that these represented sets of methylenes (δ_C 21.1, δ_H 2.32 and 1.96; δ_C 31.5, δ_H 2.07 and 1.49). One methine group (δ_C 31.7, δ_H 2.49) was observed in the HMQC spectrum, and its proton showed strong COSY correlations to the two methylene protons (δ_H 2.07 and δ_H 1.49) and medium COSY correlations to the protons

Figure 1. (a) Adult male and (b) adult female *Parectatosoma mocquerysi*. Adult males are 65−90 mm, and adult females are 90−110 mm. Photographs by Oskar V. Conle.

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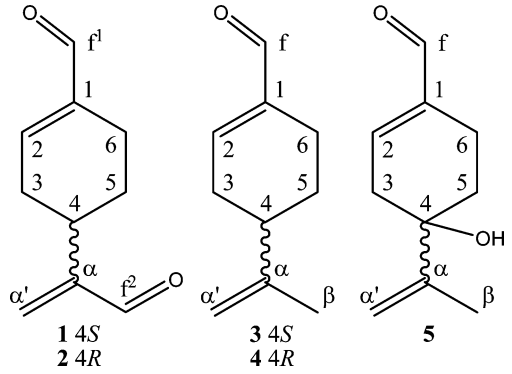
Chart 1. Structures of (4*S*)- and (4*R*)-Parectadial (*S* = **1**, *R* = **2**), (4*S*)- and (4*R*)-Perillaldehyde (*S* = **3**, *R* = **4**), and 4-Perillyl Alcohol (**5**)



of another methylene (δ_C 25.6, δ_H 1.34 and δ_H 1.02). The proton at δ 1.02 showed strong COSY correlations to those at δ 2.32 and 1.96 and a weaker correlation to the methine (δ_H 2.49). The proton at δ 1.34 showed a similarly strong COSY correlation to one at δ 1.96 and two weaker correlations to a methylene at δ 2.32 and the methine (δ_H 2.49). Weak COSY correlations between the vinyl proton at δ 5.89 and methylene protons at δ 2.32 and 1.96 suggest that they are within 4−5 bonds of one another. This set of observations completed a six-membered ring system containing one double bond.

Continued use of COSY, HMQC, HMBC, and NOESY spectra allowed preliminary elucidation of the remainder of the structure and assignment of all NMR resonances (Table 1, Supporting Information S3). Two vinyl protons (δ_H 5.18 and 5.41) were clearly on the same carbon atom (δ_C 131.8) by their correlations in the HMQC experiment. Both of those vinyl protons also showed weak COSY correlations to an aldehydic proton at δ 9.15 (δ_C 193.1). One of the vinylic protons (δ_H 5.41) showed a medium COSY correlation to the methine proton (δ_H 2.49). There is also a NOESY peak between a vinylic proton at δ 5.18 and the aldehydic proton at δ 9.15. Strong HMBC correlations between the aldehydic proton (δ_H 9.15) and a carbon (δ_C 154.3) and another between a vinylic proton (δ_H 5.18) and the same carbon, not present in the HMQC, were also observed. This suggests that there is a quaternary carbon (δ_C 154.3) to which the vinylic (δ_C 131.8), aldehydic (δ_C 193.1), and methine (δ_C 31.7) carbons are all attached. A NOESY peak was observed between the aldehydic proton at δ 9.23 and the vinylic proton at δ 5.89. Also, there is a strong HMBC correlation between the aldehydic proton at δ 9.23 and a carbon at δ 141.6. This carbon is not observed in the HMQC spectrum. These findings suggest that the second aldehyde group (δ_C 192.4, δ_H 9.23) is attached to the quaternary ring carbon. These observations provided for the assignment of structural positions for the two aldehyde and final two vinyl resonances. Thus, the structure of the major component of *P. mocquerysi* defensive spray was preliminarily assigned to structure **1**. A literature search did not reveal any previous characterization of this structure, so we named it parectadial for the genus of the organism from which it came and as a descriptor of its molecular structure in the tradition of previous phasmid insect allomone nomenclature.[2,3]

To synthetically verify the proposed structure of parectadial, perillaldehyde (available from Aldrich as enantiomerically pure *S*- or *R*-) was regiospecifically oxidized at the allylic methyl group via reflux with selenium oxide in 95% EtOH for 18 h[12−14] (Scheme 1). The synthesis gave a major product (66% yield) with identical GC retention time (15.52 min) and CIMS mass spectrum (*m*/*z* 165 $[M + H]^+$) to that of natural parectadial (Supporting Information S1). By ^{1}H NMR, the spectra of synthetic and natural parectadial lacked a methyl resonance observed in the spectrum of perillaldehyde (δ_H = 1.50, Supporting Information S4), while an additional aldehydic proton resonance was observed. ^{1}H and ^{13}C NMR spectra of both natural and synthetic parectadial were identical (Figure 2, Supporting Information S5). In order to determine the absolute

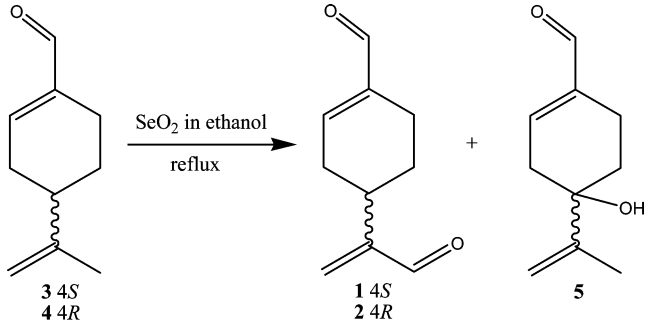
Table 1. ^{1}H and ^{13}C NMR Data of Compounds **1**, **3**, and **5** in Benzene-d_6 (ppm)

Parectadial (**1**)		
position	δ_H	δ_C
1		141.6
2	5.89	148.0
3	1.49	31.5
	2.07	
4	2.49	31.7
5	1.02	25.6
	1.34	
6	1.96	21.1
	2.32	
α		154.3
α′	5.18	131.8
	5.41	
f1	9.23	192.4
f2	9.15	193.1

Perillaldehyde (**3**)		
position	δ_H	δ_C
1		141.7
2	5.98	149.1
3	1.70	31.6
	1.88	
4	1.79	
5	1.04	26.5
	1.52	
6	1.95	21.9
	2.43	
α		148.8
α′	4.62	109.8
	4.73	
β	1.50	20.7
f	9.29	192.7

4-Perillyl Alcohol (**5**)		
position	δ_H	δ_C
1		140.6
2	5.89	147.0
3	1.89	37.7
	2.00	
4		72.1
5	1.32−1.25	31.0
	1.32−1.25	
6	2.26−2.19	18.8
	2.26−2.19	
α		150.0
α′	4.72	110.1
	4.84	
β	1.54	18.5
f	9.28	192.4

Scheme 1. Synthesis of (4*S*)- and (4*R*)-Parectadial (**1** and **2**) and 4-Perillyl Alcohol (**5**) from (4*S*)- and (4*R*)-Perillaldehyde (**3** and **4**)



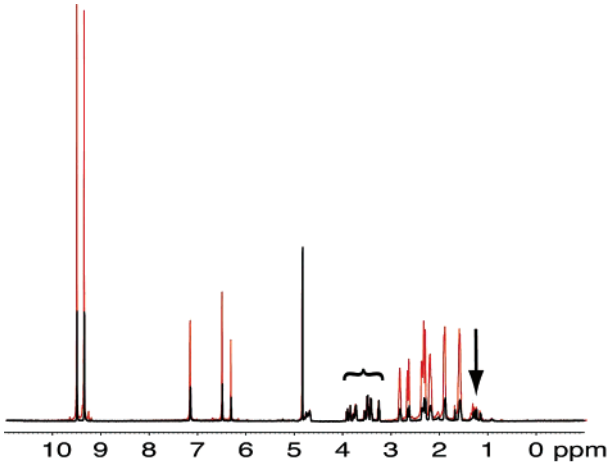


Figure 2. 1D ^{1}H NMR spectra of *P. mocquerysi* defensive spray (black) dissolved in D_2O and the same sample (red) spiked with synthetic *S*-parectadial. The bracket indicates resonances from glucose. Glucose anomeric protons were not observed due to presaturation of the corresponding region of the spectrum. The arrow indicates additional minor components in the defensive spray sample. Only resonances corresponding to parectadial increase upon spiking with synthetic material and no additional resonances appear.

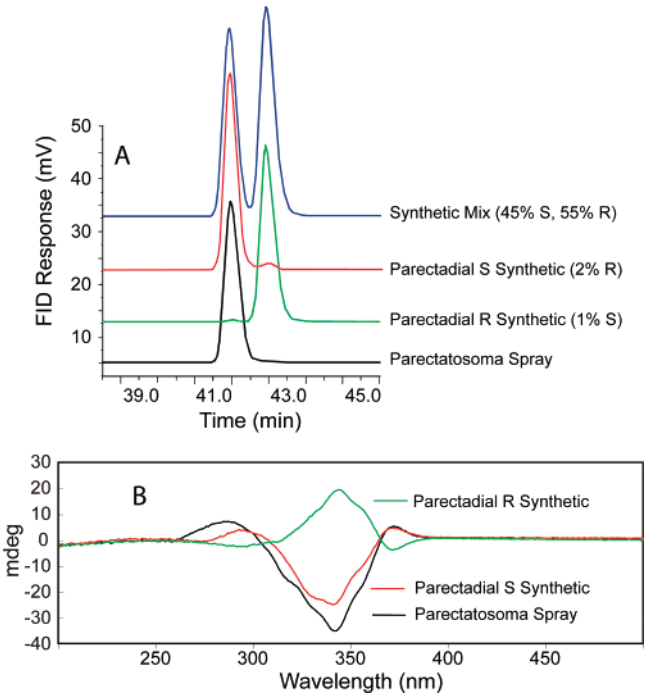


Figure 3. Absolute configuration analysis for natural parectadial. (A) Gas chromatograms (FID) of parectadial from *P. mocquerysi* (black), synthetic *R*-parectadial (green), synthetic *S*-parectadial (red), and a mixture of *R*- and *S*-parectadial (blue). (B) CD spectra of parectadial from *P. mocquerysi* (black), synthetic *S*-parectadial (red), and *R*-parectadial (green).

configuration of natural parectadial, both *S* and *R* isomers of synthetic parectadial (**1** and **2**, respectively) were compared to natural parectadial using chiral GC-FID and circular dichroism (CD). Figure 3a demonstrates that natural parectadial has an identical retention time (41.42 min) to that of synthetic *S*-parectadial (**1**) on chiral GC, which is approximately 0.5 min earlier than that of the synthetic *R*-parectadial (**2**) (41.93 min). Although not observed in the natural product, small enatiomeric impurities were present in the chromatographs of synthetic **1** and **2** that quantitatively match those from the perillaldehyde starting materials. To verify that the resolution obtained for *R* and *S* isomers was not an artifact of sample or injection conditions, a mixed sample of synthetic isomers was also analyzed, showing two peaks with retention times corresponding to those of *R*- and *S*-parectadial alone (Figure 3a). CD spectra of natural parectadial and synthetic *S*-parectadial both showed a single negative Cotton effect at 341 nm (Figure 3b). For synthetic *R*-parectadial, a positive Cotton effect was observed at 344 nm. These results show that the defensive spray samples contain only *S*-parectadial at detectable levels.

In the course of synthesizing parectadial (**1** and **2**), an additional product (**5**) (15% yield) with a GC retention time of 15.32 min and *m*/*z* 167 $[M + H]^+$ was produced via allylic oxidation of perillaldehyde (**3** and **4**). It eluted much later than parectadial using normal-phase liquid chromatography (data not shown), indicating that it was more polar. This product, which we are calling 4-perillyl alcohol, was also characterized by NMR as described in Supporting Information, S6.

There are several possible implications of this work. First, the defensive spray of *P. mocquerysi* is reported to have vesicant-like properties, causing reddening at low concentrations and eventual peeling of the skin with larger exposures (Oskar Conle, personal observation). However, no pain or itching is reported. This suggests one or more specific physiological responses to the components of the spray. Although there have been no exposures to synthetic or purified parectadial, the physiological responses following exposure to *P. mocquerysi* defensive spray are most likely due to parectadial, given its apparent chemical composition. To date, only one walkingstick insect defensive compound, dolichodial (also found in some ants[15] and at least one plant species[16]), has been investigated for its antimicrobial and antioxidant properties.[17] Second, ^{1}H NMR spectra of samples dissolved in D_2O (Supporting Information S2) indicate that the other major component observed in the defensive spray of *P. mocquerysi* is glucose. This observation is consistent with our previous study on the defensive sprays of *Anisomorpha buprestoides* (Stoll, 1813)[18] and *Peruphasma schultei* Conle and Hennemann 2005.[2] Others have provided evidence that glucoconjugate precursors are used in the biosynthesis of chrysomelidial, a monoterpenoid in the defensive secretion of leaf beetle larvae (family Chrysomelidae).[19] Together, these findings suggest that glucose may have a similar role in the defensive secretions of walkingstick insects. Finally, limonine, a compound with a similar structure to perillaldehyde and parectadial, has been identified in *Sipyloidea sipylus* (Westwood, 1859),[20] an unrelated phasmid insect from Southeast Asia.[8] These molecules possess a six-membered carbocycle, which contrasts to the five-membered carbocycles found in other species.[2,3,5,7] These similarities in allomone structure may aid future investigations of the biosynthetic pathways and evolution in walkingstick insects.

Experimental Section

General Experimental Procedures. The UV−vis absorption spectrum of *S*-parectadial was obtained using a NanoDrop ND-1000 spectrophotometer. CD spectra were collected on an Aviv-202 CD spectrometer at 25 °C over a range of 200−500 nm and a bandwidth and wavelength step size of 1 nm. For synthetic parectadial (**1** and **2**), 1 μL of synthetic product (pure oil, no solvent) was dissolved in 200 μL of $CHCl_3$ to make the final sample. For the natural parectadial sample, 10 μL of *P. mocquerysi* defensive spray was extracted with 200 μL of $CHCl_3$. NMR data were collected at 27 °C using a Bruker Avance II 600 MHz spectrometer (Bruker 600 Ultrashield magnet) equipped with a 1 mm triple-resonance high-temperature superconducting probe developed by Brey et al.[21] Acquisition parameters for all NMR experiments are available with their respective spectra in the Supporting Information.

GC-MS analysis was performed on an Agilent 6890 N gas chromatograph combined with a 5975 B ion trap mass spectrometer using either 70 eV electron impact (EI) (11 765 mV filament bias) or isobutene chemical ionization (CI). Full scan spectra were acquired over the ranges *m*/*z* 40 to 400 at 0.85 s per scan. Cool on-column injections (1 μL) were at 40 °C with He carrier gas (1.4 mL/min). The

transfer-line and manifold temperatures were 240 and 220 °C, respectively. GlasSeal connectors (Supelco Inc, Belefonte, PA) fused three columns in series: a primary deactivated column (L = 8 cm, i.d. = 0.53 mm), a HP-1MS retention gap column (L = 2 m, i.d. = 0.25 mm, df = 0.25 μm), and a J&W DB-1 analytical column (L = 30 m, i.d. = 0.25 mm, df = 0.25 μm). The oven program was as follows: isothermal at 40 °C for 5 min, heated at 11 °C/min to 200 °C, isothermal for 10 min, heated at 25 °C/min to 250 °C, and then isothermal for 15 min. Analyte retention times (min): parectadial (**1** and **2**) = 15.52 ± 0.01; perillaldehyde (**3** and **4**) = 13.23 ± 0.01; and 4-perillyl alcohol (**5**) = 15.32 ± 0.02.

Chiral GC-FID analysis was done using an Agilent 6890 N gas chromatograph equipped with a flame ionization detector (FID). Holox (Charlotte, NC) high-purity He was used as a carrier gas (1.4 mL/mn). Cool on-column injection (1 μL) at 83 °C was used; the detector was maintained at 250 °C. GlasSeal connectors (Supelco Inc.) fused three silica columns in series: a primary deactivated column (L = 8 cm, i.d. = 0.53 mm), an HP-1MS retention gap column (L = 10 m, i.d. = 0.25 mm, df = 0.25 μm), and a Supelco Beta Dex 120 analytical column (L = 30 m, i.d. = 0.25 mm, df = 0.25 μm). The oven program was as follows: isothermal at 80 °C for 5 min, heated at 7 °C/min to 150 °C, and then isothermal for 35 min. Analyte retention times (min): natural parectadial (**1**) = 41.42 ± 0.01; synthetic *S*-parectadial (**1**) = 41.42 ± 0.01; and synthetic *R*-parectadial (**2**) = 41.93 ± 0.01.

Animal Material and Sample Collection. *P. mocquerysi* has been in culture since 2003. Original stocks come from Northeast Madagascar at Ambodiriana Forest in lowland-forest habitat. Animals for this study were maintained by one of the authors (O.V.C.) in Bolsterlang, Germany. They were kept in a well-ventilated cage with about 5 cm of soil in the bottom and fed on *Hypericum* and *Eucalyptus.* Humidity was maintained at about 60−80% and temperature around 22−26 °C. Light was provided to the animals artificially for about 12 h per day. Defensive spray was collected by placing a clean 1.5 mL glass vial over the spray gland of an individual (two located just behind the head) and agitating the insect. Two independent samples (approximately 20 and 50 μL) were collected this way, each consisting of 20−40 milkings from 5 to 6 individual insects. The samples were collected about 3 months apart.

Isolation of Parectadial (1). The sample preparation of natural parectadial for NMR and other techniques involved direct addition of "crude" *P. mocquerysi* defensive spray to either D_2O (for NMR), benzene-d_6 (for NMR), MTBE (for GC-MS and GC-FID) plus 2 nL/mL tetradecane internal standard, or $CHCl_3$ for CD. The solvents listed above for analysis of natural parectadial were also used to analyze the synthetic material for each experiment listed, respectively. Parectadial was obtained as a colorless, odorless oil, spectroscopically identical to synthetic *S*-parectadial (**1**): CD ($CHCl_3$) [mdeg] (nm) −35.0 (341); HRMS m/z 165.0910 $[M + H]^+$ (calcd for $C_{10}H_{13}O_2$, 165.0910).

***S*-Parectadial Synthetic (1).** A 2.5 mmol amount of *S*-perillaldehyde (**3**) (Aldrich, 92% ee) was oxidized via reflux with 2.8 mmol of SeO_2 in 95% EtOH (5 mL) for 18 h to yield 1.56 mmol of *S*-parectadial (**1**) (66% yield); reaction progress was monitored by GC-CIMS. The reaction mixture was then filtered through Florisil to remove Se. The resulting filtrate was concentrated to an oily residue and flash chromagographed on SiO_2 (230−400 mesh) with 6:4 (v/v) hexane−EtOAc mobile phase to give a mixture of *S*-parectadial (**1**) and 4-perillyl alcohol (**5**). Utilizing an equivalent mobile phase composition (3 mL/min flow rate), HPLC with an Econosil 10 μm semipreparative silica column (Alltech 6233) stationary phase was used for final purification, as it enabled different retention for *S*-parectadial (**1**) (10.4 min) and 4-perillyl alcohol (**5**) (16.6 min). Colorless, odorless oil: UV (EtOH) λ_{max} (log ϵ) 223 (4.05); CD ($CHCl_3$) [mdeg] (nm) −25.0 (341); ^{1}H and ^{13}C NMR data, see Table 1; GC-CIMS m/z 165 $[M + H]^+$ (90.2), 147 (9.8); GC-EIMS m/z 164 $[M]^{+\bullet}$ (3), 145 (3.4), 136 (9.4), 117 (8.8), 107 (18.3), 91 (12.1), 79 (21.5), 67 (5.4), 53 (12.1), 41 (7.9); HRMS m/z 165.0895 $[M + H]^+$ (calcd for $C_{10}H_{13}O_2$, 165.0910); TLC (hexane−EtOAc, 6:4 v/v) R_f = 0.5.

***R*-Parectadial Synthetic (2).** Synthesis and purification were identical to that of *S*-parectadial (**1**), but *R*-perillaldehyde (**4**) (Aldrich, 98% ee) was used in the place of *S*-perillaldehyde (**3**). Colorless, odorless oil: CD [mdeg] (nm) 19.4 (344); HRMS m/z 165.0900 $[M + H]^+$ (calcd for $C_{10}H_{13}O_2$, 165.0910).

***S*-Perillaldehyde (3). 3** was purchased from Aldrich; 92% pure technical grade; cat# 218294-5G; odoriferous oil; ^{1}H and ^{13}C NMR data, see Table 1.

***R*-Perillaldehyde (4). 4** was purchased from Aldrich; ≥98% pure; cat# 77301-1ML; lot and filing code: 052611/1 406063373; odoriferous oil; ^{1}H and ^{13}C NMR data, see Table 1.

4-Perillyl Alcohol (5). Synthesis and purification were identical to that of *S*-parectadial (**1**). Colorless, odorless oil: ^{1}H and ^{13}C NMR data, see Table 1; GC-CIMS m/z $[MH]^+$ 167 (90.2), 147 (9.8); GC-EIMS m/z 166 $[M]^{+\bullet}$ (0.6), 148 (4.8), 138 (7.3), 123 (7.3), 109 (6.1), 105 (4.8), 84 (19.5), 69 (29.8), 55 (4.8), 41 (14.6); retention time on Econosil 10 m analytical column = 16.6 min; TLC (hexane−EtOAc, 6:4, v/v) R_f = 0.38); HRMS m/z $[M + H]^+$ 167.1060 (calcd for $C_{10}H_{13}O_2$, 167.1067).

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Supporting Information Available: GC-MS data for natural and synthetic *S*-parectadial (**1**) and 4-perillyl alcohol (**5**); full description of the characterization of 4-perillyl alcohol; all 1D ^{1}H and 2D ^{1}H and ^{13}C NMR spectra for *S*-parectadial (**1**), *S*-perillaldehyde (**3**), and 4-perillyl alcohol (**5**); and the UV−vis spectrum for synthetic *S*-parectadial. This material is available free of charge via the Internet at http://pubs.acs.org.

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