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(4E)-Dehydrocitrals [(2E,4E)- and (2Z,4E)-3,7-dimethyl-2,4,6-octatrienals] from Acarid Mite Histiogaster sp. A096 (Acari: Acaridae)

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(4*E*)-Dehydrocitrals [(2*E*,4*E*)- and (2*Z*,4*E*)-3,7-dimethyl-2,4,6-octatrienals] from Acarid Mite *Histiogaster* sp. A096 (Acari: Acaridae)†

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A mixture of two monoterpenes was obtained as the opisthonotal gland secretion from unidentified *Histiogaster* sp. A096 (Acari: Acaridae), and their structures were elucidated to be (4*E*)-dehydrocitrals [(2*E*,4*E*)- and (2*Z*,4*E*)-3,7-dimethyl-2,4,6-octatrienals] by GC/MS, GC/FT-IR, UV and ^{1}H-NMR spectra. Both isomers of (4*E*)-dehydrocitral prepared by syntheses in 4 steps from 3-methyl-2-butenal with 34.2% yields (based on the ylide) were separated by column chromatography into the (2*E*,4*E*)- and (2*Z*,4*E*)-3,7-dimethyl-2,4,6-octatrienal. Mass spectra together with GC retention times of the purified natural (4*E*)-dehydrocitrals were identical with those of synthetic (2*E*,4*E*)-3,7-dimethyl-2,4,6-octatrienal and (2*Z*,4*E*)-3,7-dimethyl-2,4,6-octatrienal. The geometry at the 2-*C* position of both synthetic (4*E*)-dehydrocitrals was confirmed by NOESY analyses. This is the first identification of (4*E*)-dehydrocitrals from the animal kingdom.

Key words: astigmatid mite; *Histiogaster* sp. A096; monoterpene aldehyde; (4*E*)-dehydrocitral; (2*E*,4*E*)- and (2*Z*,4*E*)-3,7-dimethyl-2,4,6-octatrienal

All astigmatid mites possess a pair of opisthonotal glands, from which various compounds characteristic to each species are secreted. The profile of these secretions is not only useful for identifying mite species, but is also an interesting aspect to study pheromonal functions in mites. The secretions are also interesting materials for natural product chemistry. Several compounds exhibit antifungal activities and function as various active principles such as alarm, aggregation and sex pheromones.[1] The most commonly distributed compounds among mites are monoterpenes and *n*-hydrocarbons of C_9–C_{29} length. Among 19 monoterpenes, 7 compounds have been characterized as new natural products.[1]

As a part of these investigations on substances secreted from the opisthonotal glands of astigmatid mites, we found two compounds (**1** and **2**) present in unidentified *Histiogaster* sp. A096, one of the fungivorous species. These compounds were purified, and their structures (**1** and **2**) were elucidated by spectroscopic methods and identified by synthesis as two geometrical isomers of (4*E*)-dehydrocitral, that is, (2*E*,4*E*)-3,7-dimethyl-2,4,6-octatrienal (**1**) and (2*Z*,4*E*)-3,7-dimethyl-2,4,6-octatrienal (**2**). To our knowledge, this is the first identification of (4*E*)-dehydrocitral from the animal kingdom.

Materials and Methods

Mites. Unidentified *Histiogaster* sp. A096 (Acari: Acaridae) was raised and maintained in a Petri dish (90 mm ID × 20 mm height) by feeding on dried yeast at room temperature under humid conditions in our laboratory. The species was obtained from Dr. K. Okabe of Forestry and Forest Products Research Institute (Ministry of Agriculture and Fisheries of Japan) as a line collected in the sap of *Ulmus davidiana* var. *japonica* (Ulmaceae) with a carabid beetle in Tsukuba City (Ibaraki Prefecture, Japan) by Dr. K. Tagami in June 29, 1996.

Instrumental analyses. GC analysis was performed with a Hewlett Packard 5890 series II Plus gas chromatograph with FID, using an HP-5 capillary column (0.25 mm × 30 m, 0.25 μm in film thickness, Hewlett Packard) with helium as the carrier gas at 1.23 ml/min in the split-less mode at a temperature programmed from 60°C for 2 min to 290°C at 10°C/min and then held for 5 min. GC/MS and GC/FT-IR analyses were carried out by a Hewlett Packard HP-5890 gas chromatograph/mass spectrometer operated at 70 eV in the split-less mode and by a GC/HP-5965B FT-IR spectrometer, using the column already mentioned under the same temperature program. IR spectra were recorded by a Shimadzu FTIR-8100AI spectrometer in CCl_4, UV spectra were obtained with a Beckman DU-64 spectrometer, using hexane as a solvent, and NMR spectra were measured

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with Bruker AC300 and ARX500 FT-NMR spectrometers in $CDCl_3$, using tetramethylsilane as the internal standard.

Small-scale extraction. Twenty adults of both sexes were placed in a conical tube (hand-made, 8 mm OD $\times$ 30 mm height) and extracted with hexane (4 μl) for 3 min. The extract was subsequently subjected to a GC/MS analysis. A similar extract of mites (5 mg) consisting of all stages and both sexes in hexane (100 μl), after concentration by N_2 gas, was used for measuring the GC/FT-IR spectra.

Large-scale extraction and purification. Mites (16.7 g) separated from the culture medium by shaking in a separatory funnel with brine were soaked in hexane (33 ml) for 3 min. The hexane extract (49 mg), after removing the mite bodies by filtration and concentrating *in vacuo*, was subjected to silica gel column chromatography (Wakogel C-200, 765 mg), eluting with 5 ml each of the following solvents: hexane, and a mixture of ether in hexane (1%, 3%, 5%, 7% and 10%). Compounds **1** and **2** were recovered as a mixture from the 5% and 7% ether in hexane fractions (16 mg), as monitored by GC. The mixture was further purified in an SiO_2 column (Wakogel C-200, 8.2 g), using 5% ether in hexane as the solvent, to obtain compounds **1** and **2** as yellow oil (1 mg).

Syntheses.

(E)-6-Methyl-3,5-heptadien-2-one (5). 3-Methyl-2-butenal (**3**; 8.41 g, 100 mmol) was mixed with acetylmethylenetriphenylphosphorane [$CH_3C(O)CH=PPh_3$] (**4**; 10.0 g, 31.4 mmol) in CH_2Cl_2 (25 ml), and the mixture was refluxed for 5 h while stirring. The reaction mixture, after being cooled to room temperature, was concentrated, and the resulting slurry was suspended in ether. The ether wash, after removing the crystalline precipitate by filtration and concentration, was distilled to give product **5** (*ca.* 80°C/3 mm Hg, 3.27 g, 83.8% yield) as yellow oil. GC/MS *m/z* (intensity %): 124 (M^+, 29), 110 (8), 109 (100), 81 (34), 79 (22), 77 (5), 53 (12), 43 (22), 41 (12). ^{1}H-NMR ($CDCl_3$) δ_H ppm (300 MHz): 7.42 (1H, dd, J=15.4 and 11.4 Hz, CH-C*H*=CH), 6.06 (1H, d, J=15.4 Hz, CH=C*H*-C), 6.00 (1H, d, J=11.4 Hz, C=C*H*-CH), 2.27 (3H, s, CH_3-C=O), 1.92 (3H, s, CH_3-C=), 1.90 (3H, s, CH_3-C=). ^{13}C-NMR ($CDCl_3$) δ_C ppm (75 MHz): 198.88 (C=O), 147.60 (-C=), 139.63 (-CH=), 128.03 (-CH=), 124.10 (-CH=), 27.41 ($-CH_3$), 26.66 ($-CH_3$), 19.00 ($-CH_3$).

Ethyl (4E)-3,7-dimethyl-2,4,6-octatrienoate (7). The ylide generated from triethylphosphonoacetate [$(EtO)_2P(O)CH_2CO_2Et$] (**6**; 3.60 g, 16.1 mmol) by mixing with dry THF (20 ml) in a suspension of NaH (*ca.* 60 wt%, 650 mg, 16.3 mmol) while ice-cooling in an N_2 atmosphere was coupled dropwise to compound **5** (1.00 g, 8.05 mmol) while stirring at 0°C for 1.5 h, and the mixture was then warmed to room temperature while stirring for an additional 36 h. The product was extracted with EtOAc, after being quenched with ice-cooled aqueous NH_4Cl. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The resulting crude product was purified by a silica gel column, using hexane and EtOAc (20/1) as the eluent, to yield a mixture of two isomers of **7** as yellow oil (1.03 g, 65.8%, a mixture of **7a** (70%) and **7b** (30%) by the ^{1}H-NMR spectrum).

7a. GC/MS *m/z* (intensity %): 194 (M^+, 20), 179 (4), 165 (4), 149 (14), 133 (6), 121 (100), 107 (15), 105 (41), 93 (8), 91 (27), 79 (13), 77 (14), 44 (24). ^{1}H-NMR ($CDCl_3$) δ_H ppm (300 MHz): 6.82 (1H, dd, J=15.2 and 11.2 Hz, CH-C*H*=CH), 6.15 (1H, d, J=15.2 Hz, CH=C*H*-C), 5.95 (1H, d, J=11.2 Hz, C=C*H*-CH), 5.74 (1H, s, C=C*H*-COO), 4.16 (2H, q, J=7.1 Hz, O-CH_2-CH_3), 2.33 (3H, s, CH_3-C=), 1.84 (6H, s, $(CH_3)_2$C=), 1.28 (3H, t, J=7.1 Hz, O-CH_2-CH_3). ^{13}C-NMR ($CDCl_3$) δ_C ppm (75 MHz): 167.27 (O-C=O), 153.02 (-C=), 140.27 (-C=), 133.09 (-CH=), 131.04 (-CH=), 125.33 (-CH=), 118.03 (-CH=), 59.58 (O-CH_2-), 26.41 ($-CH_3$), 18.74 ($-CH_3$), 14.37 ($2\times CH_3$-).

7b. GC/MS *m/z* (intensity %): 194 (M^+, 22), 179 (2), 165 (3), 149 (17), 133 (6), 121 (100), 107 (16), 105 (33), 93 (8), 91 (22), 79 (13), 77 (11), 43 (9). ^{1}H-NMR ($CDCl_3$) δ_H ppm (300 MHz): 7.64 (1H, d, J=15.4, CH=C*H*-C), 6.81 (1H, dd, J=15.4 and 11.1 Hz, CH-C*H*=CH), 6.05 (1H, d, J=11.1 Hz, C=C*H*-CH), 5.61 (1H, s, C=C*H*-COO), 4.16 (2H, q, J=7.1 Hz, O-CH_2-CH_3), 2.04 (3H, s, CH_3-C=), 1.84 (6H, s, $(CH_3)_2$C=), 1.28 (3H, t, J=7.1 Hz, O-CH_2-CH_3). ^{13}C-NMR ($CDCl_3$) δ_C ppm (75 MHz): 166.49 (O-C=O), 151.46 (-C=), 140.51 (-C=), 132.33 (-CH=), 127.22 (-CH=), 126.10 (-CH=), 116.10 (-CH=), 59.58 (O-CH_2-), 26.46 ($-CH_3$), 20.99 ($-CH_3$), 13.80 ($2\times CH_3$-).

(4E)-Dehydrocitral [(2E,4E)-3,7-dimethyl-2,4,6-octatrienal and (2Z,4E)-3,7-dimethyl-2,4,6-octatrienal] (1 and 2). Compound **7** (400 mg, 2.06 mmol) was reduced by $LiAlH_4$ (180 mg, 4.74 mmol) in ether (10 ml) at -10°C in an N_2 atmosphere while stirring. The mixture was further stirred at this temperature for 45 min, then quenched in ice-cooled water, and the generated precipitate was subsequently removed by filtration. The filtrate was extracted with ether. The ethereal layer, after drying over Na_2SO_4, was concentrated under a vacuum to give crude (4*E*)-3,7-dimethyl-2,4,6-octatrienol (**8**) as yellow oil (278 mg). Active MnO_2 (1.50 g, 17.3 mmol) was added to crude **8** in petroleum ether without further purification, and the mixture was

stirred at room temperature for 20 h. After removing MnO_2 by filtration, the filtrate after concentration *in vacuo* was purified in a silica gel column and separated into two products [**1**, the major product (132 mg, 42.7%) and **2**, the minor product (60 mg, 19.4%)] as yellowish viscous oil.

1. GC/MS *m/z* (intensity %): 150 (M^+, 100), 135 (59), 109 (16), 108 (29), 107 (61), 105 (28), 95 (21), 91 (62), 79 (36), 77 (24), 41 (18). IR ν_{max} (CCl_4) cm^{-1}: 2838, 2723 (aldehyde C-H bond), 1663 (conjugated aldehyde C=O bond), 1640, 1599 (conjugated double bonds). UV λ_{max} (hexane) nm (ε): 331 (39,700), 316 (42,600). ^{1}H-NMR ($CDCl_3$) δ_H ppm (500 MHz): 10.09 (1H, d, J=8.1 Hz, CH-C*H*O), 6.97 (1H, dd, J=15.2 and 11.2 Hz, CH-C*H*=CH), 6.24 (1H, d, J=15.2 Hz, CH=C*H*-C), 6.00 (1H, d, J=11.2 Hz, C=C*H*-CH), 5.94 (1H, d, J=8.1 Hz, C=C*H*-CHO), 2.30 (3H, d, J=0.8 Hz, CH-C(C*H*$_3$)=CH), 1.87 (6H, s, (C*H*$_3$)$_2$C=). ^{13}C-NMR ($CDCl_3$) δ_C ppm (125 MHz): 191.10 (CH-*C*HO), 155.17 (CH-*C*(CH$_3$)=CH), 142.45 ((CH$_3$)$_2$*C*=), 132.63 (CH-*C*H=CH), 132.52 (CH=*C*H-C), 128.64 (C=*C*H-CHO), 125.39 (C=*C*H-CH), 26.48 (*C*H$_3$-C=), 18.85 (*C*H$_3$-C=), 13.05 (CH-C(*C*H$_3$)=CH).

2. GC/MS *m/z* (intensity %): 150 (M^+, 100), 135 (60), 109 (20), 108 (30), 107 (84), 105 (32), 95 (22), 91 (80), 79 (54), 77 (36), 41 (28). IR ν_{max} (CCl_4) cm^{-1}: 2857, 2734 (aldehyde C-H bond), 1673 (conjugated aldehyde C=O bond), 1640, 1603 (conjugated double bonds). UV λ_{max} (hexane) nm (ε): 329 (23,700), 314 (27,000). ^{1}H-NMR ($CDCl_3$) δ_H ppm (500 MHz): 10.18 (1H, d, J=8.0 Hz, CH-C*H*O), 7.14 (1H, d, J=15.1 Hz, CH=C*H*-C), 6.87 (1H, dd, J=15.1 and 11.1 Hz, CH-C*H*=CH), 6.03 (1H, d, J=11.1 Hz, C=C*H*-CH), 5.82 (1H, d, J=8.0 Hz, C=C*H*-CHO), 2.12 (3H, d, J=0.9 Hz, CH-C(C*H*$_3$)=CH), 1.88 (3H, s, C*H*$_3$-C=), 1.87 (3H, s, C*H*$_3$-C=). ^{13}C-NMR ($CDCl_3$) δ_C ppm (125 MHz): 189.93 (CH-*C*HO), 155.07 (CH-*C*(CH$_3$)=CH), 142.64 ((CH$_3$)$_2$*C*=), 133.58 (CH-*C*H=CH), 127.43 (C=*C*H-CHO), 125.42 (C=*C*H-CH), 124.37 (CH=*C*H-C), 26.48 (*C*H$_3$-C=), 21.15 (CH-C(*C*H$_3$)=CH), 18.83 (*C*H$_3$-C=).

Results

The results of the GC and GC/MS analyses of the mite hexane extract are summarized in Table 1. The GLC profile showed two unidentified peaks (**1**: t_R=11.89 min and **2**: t_R=11.56 min), together with five other components; 2-heptanone (t_R=4.05 min), benzaldehyde (t_R=5.15 min), rosefuran [2-(3-methyl-2-butenyl)-3-methylfuran] (t_R=7.30 min), 3-hydroxybenzene-1,2-dicarbaldehyde (t_R=10.18 min) and tridecane (t_R=10.26 min). All compounds from the mite, except **1** and **2**, were identified by comparing their GC retention times and mass spectra with those of standards commercially available or prepared by synthesis. GC/MS analyses of both compounds **1** and **2** indicated the molecular and base ions at the same *m/z* 150, this being indicative of highly conjugated compounds possessing a molecular formula of $C_{10}H_{14}O$, together with a similar set of the following fragment ions: 135, 109, 108, 107, 105, 95, 91, 79, 77 and 41 (Table 1). Compounds **1** and **2** also exhibited the same set of characteristic bands by GC/FT-IR: 2834 and 2726 cm^{-1} (aldehyde C-H bond), and 1689 cm^{-1} (conjugated aldehyde C=O bond). Analyses by GC/MS and GC/FT-IR indicated **1** and **2** to be isomeric α,β-unsaturated aldehydes. The NMR spectrum of a mixture (1 mg) of **1** and **2** purified from the mite extract (consisting of all developmental stages, 16.7 g) indicated two sets of proton signals (major **1**/minor **2**=78/22) as summarized in Table 2. A pair of coupled chemical shifts at δ 10.10 (an aldehydic proton, 1H, d, J=8.1 Hz) and at δ 5.95 (an olefinic proton, 1H, d, J=8.1 Hz) support the presence of a conjugated aldehyde moiety in the molecule of **1**. Two methyls at δ 1.87 (6H, s) and one methyl at δ 2.30 (3H, s) were concluded to be connected with sp^2 carbons with no proton substitution. Three other olefinic protons at δ 6.97 (1H, dd, J=15.2 and 11.2 Hz), δ 6.24 (1H, d, J=15.2 Hz) and δ 6.00 (1H, d,

Table 1. GC/MS Data for Compounds Obtained from the Hexane Extract of *Histiogaster* sp. A096: GC Retention Times, Molecular and Diagnostic Ions, and Relative Abundance

Compounds observed	GC t_R (min)	Relative abundance (%)	Molecular and diagnostic ions *m/z* (intensity %)
2-Heptanone	4.05	6.9	43(100), 58(87), 59(14), 71(23), 72(6), 85(5), 99(6), 114(M^+, 17)
Benzaldehyde	5.15	11.5	50(13), 51(24), 77(78), 78(12), 105(93), 106(M^+, 100)
Rosefuran	7.30	3.8	41(14), 79(22), 82(18), 91(27), 95(22), 105(13), 107(25), 135(90), 150(M^+, 100)
3-Hydroxybenzene-1,2-dicarbaldehyde	10.18	6.8	63(8), 65(22), 93(39), 121(100), 122(59), 150(M^+, 78)
Tridecane	10.26	47.5	41(26), 43(63), 57(100), 71(73), 85(52), 98(12), 99(16), 113(12), 127(11), 141(8), 184(M^+, 16)
Compound **2**	11.56	7.9	41(23), 77(26), 79(37), 91(68), 95(24), 105(29), 107(68), 108(33), 109(20), 135(56), 150(M^+, 100)
Compound **1**	11.89	15.7	41(20), 77(26), 79(38), 91(63), 95(22), 105(28), 107(63), 108(31), 109(22), 135(60), 150(M^+, 100)

Table 2. ^{1}H-NMR Spectral Data for Compounds **1** and **2** from *Histiogaster* sp. A096

Compound **1**				Compound **2**			
δ (ppm)	J (Hz)		proton	δ (ppm)	J (Hz)		proton
10.10	d	8.1	1H, CH-C*H*O	10.18	d	8.0	1H, CH-C*H*O
6.97	dd	15.2	1H, CH-C*H*=CH	7.14	d	15.1	1H, CH=C*H*-C
		11.2		6.87	dd	15.1	1H, CH-C*H*=CH
6.24	d	15.2	1H, CH=C*H*-C			11.1	
6.00	d	11.2	1H, C=C*H*-CH	6.03	d	11.1	1H, C=C*H*-CH
5.95	d	8.1	1H, C=C*H*-CHO	5.82	d	8.0	1H, C=C*H*-CHO
2.30	d	0.8	3H, CH_3-C=	2.12	d	0.9	3H, CH_3-C=
1.87	s		6H, $(CH_3)_2$C=	1.88	s		3H, CH_3-C=
				1.87	s		3H, CH_3-C=

J = 11.2 Hz) were coupled each other, which also supports the conjugated diene system. The coupling constant (J = 15.2 Hz) between two protons at δ 6.97 and δ 6.24 suggests *E*-geometry of the carbon-carbon double bond at the 4-*C* position. These partial structures enabled major isomer **1** to be elucidated as either the (2*E*)- or (2*Z*)-isomer of (4*E*)-dehydrocitral [(2*E*,4*E*)- or (2*Z*,4*E*)-3,7-dimethyl-2,4,6-octatrienal], although the geometry of the carbon-carbon double bond at the 2-*C* position was obscure. The structure of **2** was also likewise elucidated and concluded to be the other isomer as already mentioned. As a result, **1** and **2** were deduced to be both 2-*C* geometric isomers of (4*E*)-dehydrocitral. The UV spectrum of the mixture showed absorption maxima at 331 and 316 nm, supporting the conjugated triene structure with an aldehyde group.

The synthesis of (4*E*)-dehydrocitral was accomplished in four steps from 3-methyl-2-butenal (**3**) and acetylmethylenetriphenylphosphorane [$CH_3C(O)CH=PPh_3$] (**4**) as starting materials (Fig. 1). The Wittig reaction of **3** with **4** exclusively gave the conjugated ketone (*E*)-6-methyl-3,5-heptadien-2-one (**5**). The Hornor-Wadsworth-Emmons reaction of ketone **5** with the ylide generated from triethylphosphonoacetate [$(EtO)_2P(O)CH_2CO_2Et$] (**6**) with sodium hydride afforded the monoterpene ester, ethyl (4*E*)-3,7-dimethyl-2,4,6-octatrienoate (**7**), consisting of two isomers **7a** and **7b** (**7a**/**7b** = 70/30 by ^{1}H-NMR) whose 2-*C* geometry was not determined. Ester **7**, without separating the two isomers, was successfully reduced by $LiAlH_4$ with none of the irregular reaction that was expected.[2] The resulting crude oil, containing (4*E*)-3,7-dimethyl-2,4,6-octatrienol (**8**), was oxidized by an excess of active MnO_2, and then (4*E*)-dehydrocitral was obtained as a mixture of two isomers which were separated in a silica gel column. The overall yield of (4*E*)-dehydrocitral based on **4** was 34.2%; major product **1** (23.5% yield) and minor product **2** (10.7% yield). The GC retention times and spectral data showed the major and the minor products to be respectively identical to natural **1** and **2**. The C-H relationship was examined by H-H COSY, HMQC and HMBC, and the 2-*C* geometry

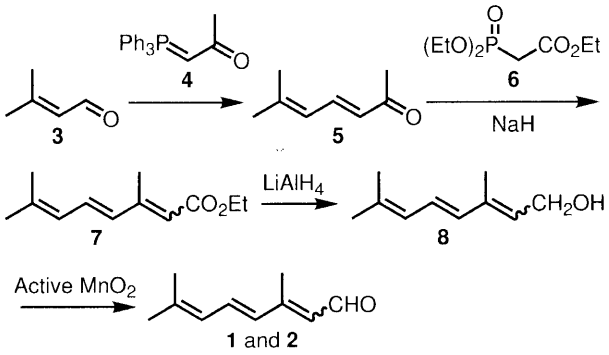

Fig. 1. Synthetic Route to (4*E*)-Dehydrocitral (**1** and **2**).

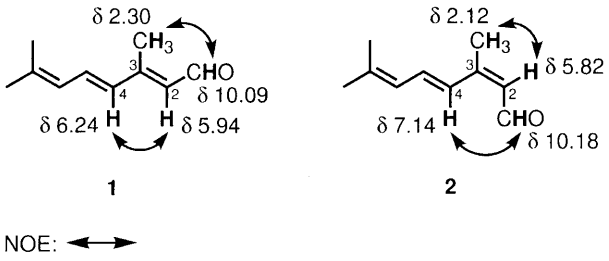

Fig. 2. NOE Correlations in Synthetic **1** and **2**.

was established by NOESY analyses. NOE correlations were confirmed between the methyl at δ 2.30 and aldehyde proton at δ 10.09, and between two vinyl protons at δ 5.94 and δ 6.24 in synthetic **1**, while synthetic **2** indicated the other two sets of correlations between an aldehyde proton (δ 10.18) and a vinyl proton at δ 7.14, and a methyl at δ 2.12 and a vinyl at δ 5.82 (Fig. 2). As a result, natural product **1** was identified as (2*E*,4*E*)-3,7-dimethyl-2,4,6-octatrienal, and **2** as (2*Z*,4*E*)-3,7-dimethyl-2,4,6-octatrienal.

Discussion

Dehydrocitral as a natural product has been identified from the following three plant species in the family Asteraceae (=Compositae): *Ambrosia confertiflora*, where the (2*E*,4*E*)-isomer has been stated

without any conclusive evidence,[3] *Artemisia douglasiana*, from which the isomer has also been detected,[4] and *Laggera tomentosa*, in which the (2*E*,4*E*)- and (2*Z*,4*E*)-isomers have been demonstrated based on ^{1}H-NMR data, along with three other monoterpenes.[5] An analogous ester, dehydroneryl isovalerate [(2*Z*,4*E*)-3,7-dimethyl-2,4,6-octatrienyl 3-methylbutyrate] has been reported from *Anthemis montana* (Asteraceae), which has been characterized by hydrolysis and subsequent oxidation into dehydroneral, the (2*Z*,4*E*)-isomer of dehydrocitral, in which the (4*E*)-geometry was evident by the coupling constant (15 Hz).[6] Dehydrocitral theoretically possesses four geometrical isomers, (2*E*,4*E*), (2*Z*,4*E*), (2*E*,4*Z*) and (2*Z*,4*Z*), among which only two isomers of the (4*E*)-type, that is, (2*E*,4*E*) and (2*Z*,4*E*), have previously been reported from plants. On the other hand, none of the dehydrocitral isomers have hitherto been detected in the animal kingdom. It is interesting that the same mixture of geometrical isomers of dehydrocitral present as plant components were identified from mite species *Histiogaster* sp. A096. No trace of *Z*-geometrical isomers at the 4-*C* position was detectable or suggested by the GC/MS analysis of the mite hexane extract, nor by the ^{1}H-NMR analysis of the purified dehydrocitral fraction by SiO_2 column chromatography.

The GC profile of *Histiogaster* sp. A096 indicated the presence of characteristic compounds other than **1** [(2*E*,4*E*)-3,7-dimethyl-2,4,6-octatrienal] and **2** [(2*Z*,4*E*)-3,7-dimethyl-2,4,6-octatrienal]; that is, 2-heptanone and benzaldehyde which have not been detected among the other 51 species of astigmatid mites so far investigated.[1] These compounds, therefore, are useful chemotaxonomical cues to identify the species. 2-Heptanone and benzaldehyde are well-known compounds among Insecta and Millipeds.[7,8]

Several facile methods to synthesize various polyenals including dehydrocitral have recently been established.[9-11] However, we chose a more practical method, starting from readily available materials, to identify the structures of **1** and **2**. In our synthetic procedure, no trace of (4*Z*)-isomers was produced, because a resonance-stabilized alkylidenetriphenylphosphorane (**4**) was used for preparing **5**, whereby the reaction proceeded as theoretically expected.[12]

The geometry at the 2-*C* position of **1** and **2** was unambiguously determined by a NOESY experiment on the synthetic samples. The chemical shift data of the 4-*C* olefinic proton in the ^{1}H-NMR spectrum also characteristically differed between the two isomers; (2*E*,4*E*)-isomer (**1**) at δ 6.24 and (2*Z*,4*E*)-isomer (**2**) at δ 7.14.

In this study, (4*E*)-dehydrocitrals (**1**; (2*E*,4*E*)-3,7-dimethyl-2,4,6-octatrienal and **2**; (2*Z*,4*E*)-3,7-dimethyl-2,4,6-octatrienal) have been demonstrated as mite components. Their biological functions such as semiochemicals for the mite are now being investigated.

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