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Gomadalactones A, B, and C: novel 3-oxabicyclo[3.3.0]octane compounds in the contact sex pheromone of the white-spotted longicorn beetle, *Anoplophora malasiaca*

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Abstract—The ether extract of the females of white-spotted longicorn beetle *Anoplophora malasiaca* showed activity as contact sex pheromone to males. The extract was fractionated, and a pheromonal activity was revealed only when three fractions; *n*-hexane, *n*-hexane/EtOAc 9:1, and EtOAc were blended. The relative structures of gomadalactone A, B, and C, three active components isolated from the EtOAc fraction, were determined by spectroscopic studies to be (1*S**,4*R**,5*S**)-5-hydroxy-4-[(*E*)-7-hydroxy-4-methylhept-3-enyl]-4,8-dimethyl-3-oxabicyclo[3.3.0]octan-7-en-2,6-dione, (1*R**,4*R**,5*R**)-5-hydroxy-4-[(*E*)-7-hydroxy-4-methylhept-3-enyl]-4,8-dimethyl-3-oxabicyclo[3.3.0]octan-7-en-2,6-dione, and (1*S**,4*R**,5*S**,8*S**)-5-hydroxy-4-[(*E*)-7-hydroxy-4-methylhept-3-enyl]-4,8-dimethyl-3-oxabicyclo[3.3.0]octan-2,6-dione, respectively.

The white-spotted longicorn beetle *Anoplophora malasiaca* (Thomson) (Coleoptera: Cerambycidae) (in Japanese, 'gomadara-kamikiri') is a serious pest of various arbor species, including citrus, apple, pear, and willow.[1] The mating sequence and evidence for contact sex pheromone are well studied in this species.[2,3]

During intensive clarification and identification of the female contact pheromone components with the use of a male *A. malasiaca* bioassay, we found that pheromonal activity equaled to that of ether extract of females was revealed only when three of the six fractions obtained by silica gel column fractionation of the ether extract of the female body, that is *n*-hexane, *n*-hexane/EtOAc 9:1, and EtOAc fractions were blended. EtOAc fraction was essential to evoke a series of precopulatory behaviors of males toward a glass dummy when coated together with *n*-hexane and *n*-hexane/EtOAc 9:1 fractions (58% of males responded, $N = 40$), since when the blend without the EtOAc fraction was coated to a dummy, only 8% of the males responded to it. We have already identified the active components in the former two fractions (eight hydrocarbons and five ketones, respectively).[3,4] We describe here the isolation and structural study of three novel active compounds gomadalactones, A (**1**), B (**2**), and C (**3**), found in the latter EtOAc fraction.

The ether extract of 200 females was chromatographed on silica gel column with *n*-hexane, *n*-hexane/EtOAc 9:1, 8:2, 5:5, and EtOAc, and then washed with methanol. The EtOAc, fraction was performed by HPLC (Cosmosil AR-II, 250×4.6 mm, MeOH/H_2O 52:48), and three active compounds **1**–**3** were successively eluted. When the HPLC fractions including those compounds were individually coated to a dummy together with *n*-hexane and *n*-hexane/EtOAc 9:1 fractions, ca. 10–55% of males responded. These compounds were isolated as colorless amorphous solids, <0.2 mg. They are soluble in methanol but insoluble in EtOAc and $CHCl_3$.

From the analyses of NMR, MS, UV, and CD spectra, we determined compounds **1** and **2** were diastereomers of substituted 3-oxabicyclo[3.3.0]oct-7-ene and compound **3** a substituted 3-oxabicyclo[3.3.0]octane. On

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account of their structural novelty and importance for the unique bioactivity, we named them gomadalactones A (**1**), B (**2**), and C (**3**), and report here detailed structure elucidation below.

Gomadalactones A (**1**) and B (**2**) show $\pi \rightarrow \pi^*$ transition at 220 and 240 nm (shoulder) in UV and have a molecular formula of $C_{17}H_{24}O_5$,[5,6] while gomadalactone C (**3**) has a $C_{17}H_{26}O_5$ with no UV band in the corresponding region.[7] It was expected that gomadalactones A (**1**) and B (**2**) have conjugated double bonds and gomadalactone C (**3**) has a saturated structure of (**1**) or (**2**).

These compounds have a same side chain structure that was confirmed to be a (*E*)-7-hydroxy-4-methylhept-3-enyl unit by the signals in ^{1}H and ^{13}C NMR at an early stage (Tables 1 and 2). The *E*-configuration of the side chain was indicated by chemical shifts, C-3′, 4′-Me,

Table 1. ^{1}H and ^{13}C NMR data[a] for gomadalactone A (**1**) and B (**2**)

C/H no.	Gomadalactone A (**1**)			Gomadalactone B (**2**)		
	δ_H mult. (*J* in Hz)	HMBC (C)	δ_C	δ_H mult. (*J* in Hz)	HMBC (C)	δ_C
1	3.668 br q (1.1)	2, 5, 7, 8	61.27	3.666 br q (1.1)	2, 5, 8	61.88
2			172.96			173.07
4			91.27			90.32
5			84.56			84.62
6			206.38			206.31
7	6.027–6.031 m	1, 5, 6, 8, 8-Me	130.56	6.026–6.030 m	1, 5, 6, 8-Me	130.37
8			174.41			174.39
4-Me	1.464 s	4, 5, 1′	21.41	1.274 s	4, 5, 1′	23.40
8-Me	2.294 dd (1.4, 1.1)	1, 2, 6, 7, 8	17.76	2.291 dd (1.4, 1.1)	1, 6, 7, 8	17.71
1′	1.445 ddd (14.2, 11.7, 7.1)	4, 5, 4-Me, 2′, 3	39.24	1.815 ddd (14.2, 11.2, 5.5)	4, 5, 2′, 3	38.23
	1.707 ddd (14.2, 11.6, 5.3)	4, 5, 4-Me, 2′, 3		1.849 ddd (14.2, 11.1, 5.2)	4, 5, 2′, 3′	
2′	1.99–2.04 m	1′, 3′, 4′	23.54	2.133 dddd (14, 11.1, 7.2, 5.2)	3′, 5′	23.51
	2.13–2.18 m	4, 1′, 3′, 4′		2.179 dddd (14, 11.2, 7.2, 5.5)	3′, 5′	
3′	5.070 ddq (7.2, 7.2, 1.1)	2′, 5′, 4′-Me	124.58	5.186 ddq (7.2, 7.2, 1.2)	1′, 2′, 5′, 4′-Me	124.93
4′			136.48			136.38
5′	2.000 br 1 (7.8)[b]	3′, 4′, 6′, 7′, 4′-Me	36.70	2.034 br t (7.5)[b]	3′, 4′, 6′, 7′, 4′-Me	36.74
6′	1.587 tt (7.8, 6.6)[b]	4′, 5′, 7′	31.82	1.617 ddt (7.8, 7.6, 6.7)[b]	4′, 5′, 7′	31.87
7′	3.494 t (6.7)[b]	5′, 6′	62.58	3.518 t (6.7)[b]	5′, 6′	62.61
4′-Me	1.582 br s	3′, 4′, 5′	15.83	1.632 br s	3′, 4′, 5′	15.90

[a] 800.1 MHz for ^{1}H and 125.8 MHz for ^{13}C, in CD_3OH (δ_H 3.30, δ_H 49.0) at 298 K.
[b] Two protons were equivalently observed.

Table 2. ^{1}H and ^{13}C NMR data[a] for gomadalactone C (**3**)

C/H no.	Gomadalactone C (**3**)		
	δ_H mult. (*J* in Hz)	HMBC (C)	δ_C
1	3.135 dd (7.5, 1.6)	2, 5, 6, 7, 8	54.17
2			174.94
4			88.95
5			86.21
6			215.51
7_{ax}	2.038 dd (17.0, 14.1)	6	47.22
7_{eq}	2.469 ddd (17.0, 6.2, 1.7)	1,5, 6, 8-Me	
8	2.555 dddq (14.1, 7.5, 6.2, 6.9)	1, 2, 7, 8-Me	31.21
4-Me	1.390 s	4, 5, 1′	21.92
8-Me	1.333 d (6.9)	1, 7, 8	15.48
1′	1.417 ddd (14.2, 11.7, 4.8)	4-Me, 2′, 3′	37.54
	1.722 ddd (14.2, 11.8, 5.1)	2′, 3′	
2′	2.015 ddd (13.8, 11.8, 7.2, 4.8)	1′, 3′, 4′	23.56
	2.242 dddd (13.8, 11.7, 7.2, 5.1)	1′, 3′	
3′	5.111 tq (7.2, 1.2)	1 ′, 2′, 5′, 4′-Me	124.82
4′			136.30
5′	2.018 br t (7.7)[b]	4′, 6′, 7′, 4′-Me	36.74
6′	1.604 ddt (8.1, 7.3, 6.7)[b]	5′, 7′	31.85
7′	3.508 t (6.7)[b]	5′, 6′	62.61
4′-Me	1.619 br s	3′, 4′	15.87

[a] 800.1 MHz for ^{1}H and 125.8 MHz for ^{13}C, in CD_3OH (δ_H 3.30, δ_C 49.0) at 298 K.
[b] Two protons were equivalently observed.

and C-5′, and NOESY correlations, H-3′/H-5′and 4′-Me/H-2′, as shown in Figure 1.

Gomadalactone A (**1**) showed NMR signals at δ_H 2.294/δ_C 17.76 (8-Me), δ_H 3.668/δ_C 61.27 (H/C-1) and δ_H 6.027–6.031/δ_C 130.56 (H/C-7) that consist a weakly coupled AMX_3 ^{1}H-spin system clarified by the direct reading of *J*-values (Table 1) and cross-peaks on DQF-COSY experiment. HSQC and HMBC experiments allowed to correlate several ^{13}C signals including δ_C 206.38 (C-6 carbonyl), δ_C 130.56 (C-7 α-olefin, methine), δ_C 174.41 (C-8 β-olefin, quaternary), and δ_C 84.56 (C-5, O-substituted quaternary). The key assignment in this compound was finding the strongly downfield shifted olefin signal at δ_C 174.41, indicating both C=O and C=C were in a coplanar configuration due to ring geometry, that is β-methyl-α,β-unsaturated cyclopentenone structure. These chemical shifts were very similar to the reported value at enone moiety of 3-methyl-2-cyclopentenone: δ_C 209.5 (C=O), 130.5 (α-olefin methine), 178.9 (β-olefin, quaternary), 19.3 (β-methyl).[8] The signals δ_H 3.668/δ_C 61.27 (H/C-1) and δ_C 84.56 (C-5, O-substituted quaternary), assigned to γ- and δ-position of the cyclopentenone structure, were slightly different from the above reference data due to substitution. The methyl signals at δ_H 1.464/δ_C 21.41 (4-methyl) and methylene signals at δ_H 1.707 and 1.445/δ_C 39.24 (1′-methylene) showed HMBC correlation each other. Additionally, these ^{1}H signals were correlated with the signals at δ_C 91.27 (C-4) and δ_C 84.56 (C-5) by HMBC experiment. So, the methyl group and the side chain were on the O-substituted

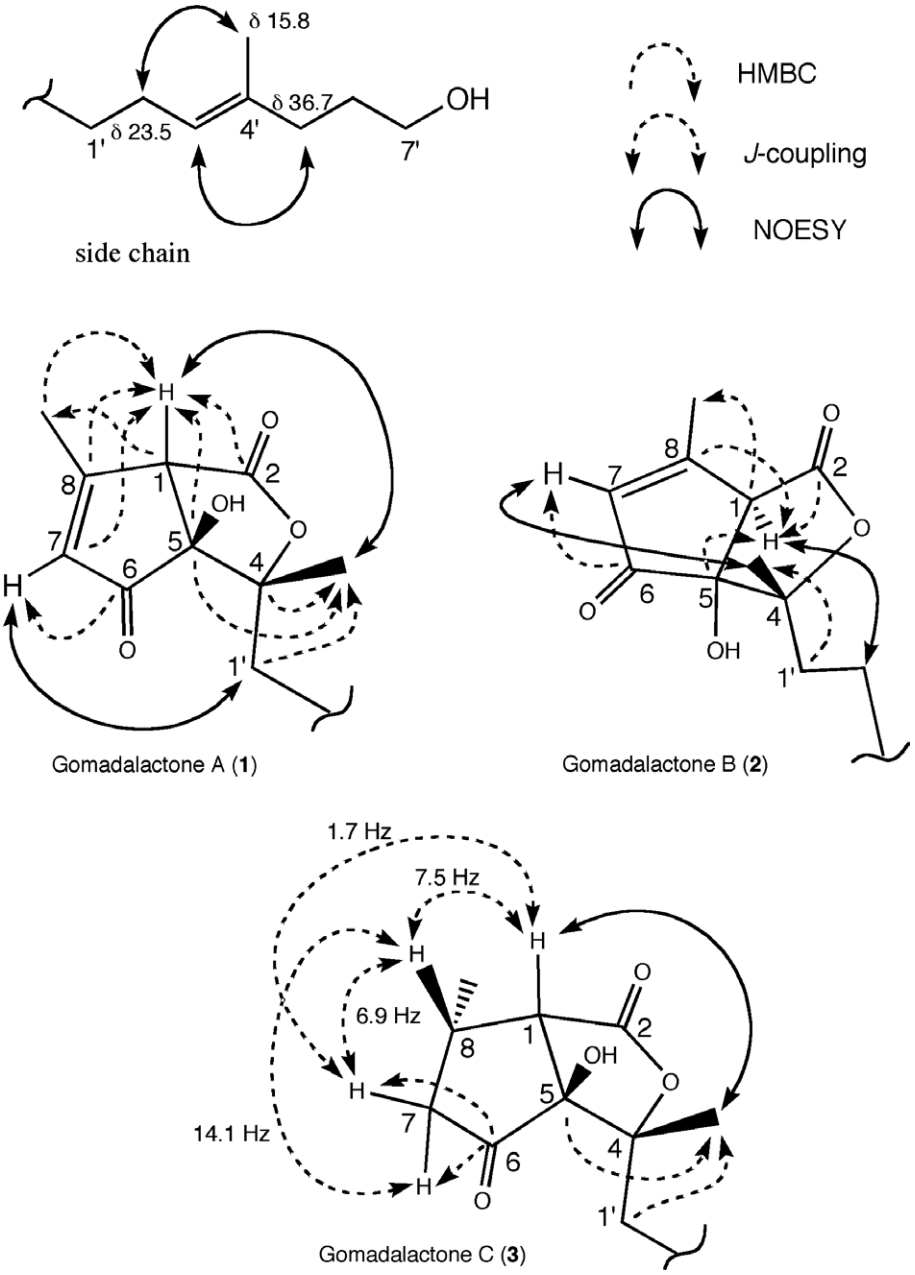
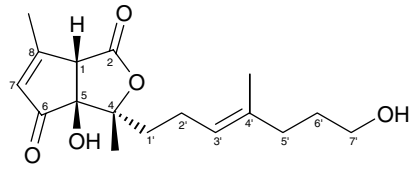


Figure 1. Key correlations, selected δ_C and $J_{H,H}$-values observed in the NMR experiments for gomadalactones A (**1**), B (**2**), and C (**3**).

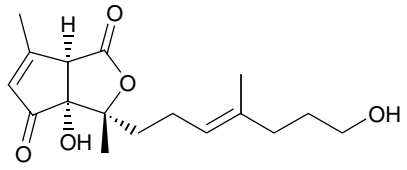
quaternary carbon at δ_C 91.27 (C-4) that bonded to the O-substituted quaternary carbon at δ-position of the cyclopentenone, δ_C 84.56 (C-5).

The remaining quaternary carbon observed at δ_C 172.96 (C-2) ,that correlated to the ^{1}H signal at δ_H 3.668 (δ_C 61.27, H/C-1), was assigned as a lactone carbonyl carbon attached to C-1 and O-4, considering the O-substituted quaternary carbons at near position and the downfield shift at C-4, δ_C 91.27. By the elementary composition calculated by HRMS analysis,[5] the substituent at C-5 should be a hydroxyl group. The NOESY correlations, 4-Me/H-1 and H-1′/H-7, clarified the steric relation between ring juncture and chiral center at C-4 position, in which the side chain and Me-4 were *endo* and *exo* positions, respectively (Fig. 1). Thus, gomadalactone A (**1**) was determined to be (1*S**,4*R**, 5*S**)-5-hydroxy-4-[(*E*)-7-hydroxy-4-methylhept-3-enyl]-4,8-dimethyl-3-oxabicyclo[3.3.0]octan-7-en-2,6-dione as shown in Figure 2.

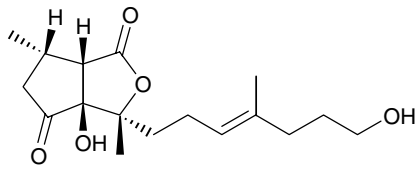
The structural analysis of gomadalactone B (**2**), examined by the molecular formula determined by the HRMS measurement[6] and NMR assignments based on through-bond interaction such as DQF-COSY, HSQC, HMBC experiment (Table 1), led exactly the same structure as that of gomadalactone A (**1**). As compared to compound **1**, some specific chemical shifts around C-4 were different as follows: $\Delta\delta_C$ −0.95 at C-4, $\Delta\delta_H$ −0.190/$\Delta\delta_C$ +1.99 at H/C-4-Me, $\Delta\delta_H$ −0.108, +0.404/$\Delta\delta_C$ −1.01 at H/C-1′, $\Delta\delta_H$ −0.138 at H-2′, $\Delta\delta_H$ −0.116 at H-3′. The NOESY correlation uncovered the through-space interactions, Me-4/H-7 and H-2′/H-1 that showed the steric relationship at C-4 was opposite of (**1**), that is the side chain was *exo* and the 4-Me *endo*. Hence, gomadalactone B (**2**) was determined to be (1*R**,4*R**,5*R**)-5-hydroxy-4-[(*E*)-7-hydroxy-4-methylhept-3-enyl]-4,8-dimethyl-3-oxabicyclo[3.3.0]octan-7-en-2,6-dione as shown in Figure 2.



Gomadalactone A (**1**)



Gomadalactone B (**2**)



Gomadalactone C (**3**)

Figure 2. Relative structures of gomadalactones A (**1**), B (**2**), and C (**3**).

The ^{13}C spectra of gomadalactone C (**3**) showed several signals similar in chemical shifts to those of the side chain and the lactone ring of gomadalactone A (**1**) and B (**2**) (Table 1). The ^{1}H signals correlated with these ^{13}C signals by HSQC were more like to those of gomadalactone A (**1**), especially at 4-Me ($\Delta\delta_H$ −0.070) and 1′-methylene ($\Delta\delta_H$ +0.015 and −0.028) as compared to those of gomadalactone B (**2**) at which $\Delta\delta_H$ +0.116 (4-Me), −0.127 and −0.398 (1′-methylene). Therefore, the gomadalactone C (**3**) seemed to contain γ-lactone substructure substituted with a methyl group, hydroxy group, and the same side chain. The hydroxyl group at β-position might be the same steric geometry as gomadalactone A (**1**), since its magnetic anisotropy possibly affected the geminal protons at the 1′-methylene. The data of DQF-COSY and HSQC experiments indicated that the compound **3** had a set of ^{1}H-spin system besides the above, attached each on sp^3 carbons, at δ_H 3.135/δ_C 54.17 (H/C-1), δ_H 2.555/δ_C 31.21 (H/C-8), δ_H 1.333/δ_C 15.48 (Me-8), δ_H 2.038, and 2.469/δ_C 47.22 (H/C-7). The HMBC correlations from quaternary carbons observed at δ_C 174.94 (C-2, lactone carbonyl), 215.51 (C-6, carbonyl), 88.95 (C-4), and 86.21 (C-5) to the above ^{1}H signals clarified the β-methylcyclopentanone substructure that adjacent to the lactone moiety to consist 3-oxabicyclo[3.3.0]octane skeleton. The W-type *J*-coupling observed between δ_H 3.135 (H-1) and δ_H 2.469 (H-7$_{eq}$) ($J = 1.7$ Hz) indicated those two protons consisted of 1,3-pseudo equatorial conformation. A large coupling constant, 14.1 Hz, observed between vicinal protons δ_H 2.038 (H-7$_{ax}$) and δ_H 2.555 (H-8), indicated that these two protons occupied a 1,2-pseudo axial position. The NOESY correlation observed between δ_H 3.135 (H-1) and δ_H 1.390 (4-Me) indicated H-1 and 4-Me were on the same side. The steric geometry, the 4-Me *exo* and the 8-Me *endo*, was consistent with the chemical shift similarity at side chain between gomadalactone (A) and (C). Thus, the gomadalactone C (**3**) was determined to be (1*S**,4*R**,5*S**,8*S**)-5-hydroxy-4-[(*E*)-7-hydroxy-4-methylhept-3-enyl]-4,8-dimethyl-3-oxabicyclo[3.3.0]octan-2,6-dione as shown in Figure 2.

In the proposed structure of gomadalactones A (**1**) and B (**2**), H-1 occupied both a γ-position of cyclopentenone and an α-position of γ-lactone carbonyl, and the high acidity of H-1 was expected. Dissolving in CD_3OD, the ^{1}H signal of H-1 disappeared in NMR, and mass analysis of recovered compounds showed one mass unit greater *m*/*z* value than that without CD_3OD treatment. This phenomenon was explained by H/D exchange process at the H-1 position and supported the proposed structures.

The CD spectra of gomadalactone A (**1**) exhibited first positive and second negative Cotton curves (Fig. 3; λ_{ext} 242.8 nm (θ +83.4 mdeg), λ_{ext} 219.2 nm (θ −106.5 mdeg))[5] that were probably caused by an interaction including

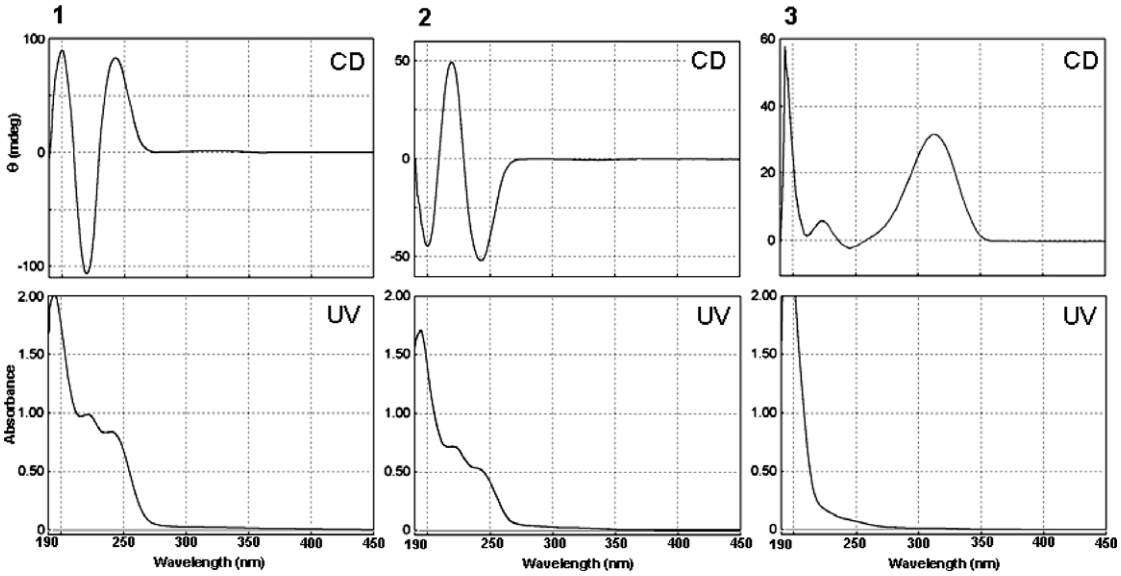


Figure 3. CD and UV spectra of gomadalactones A (**1**), B (**2**), and C (**3**). They were recorded in methanol using 1 mm cell with the same concentration in each pair.

split two $\pi \rightarrow \pi^*$ transitions at 222 and 240 nm, arising from distorted enone moiety. However, it was difficult to discern directions of the UV transitions with enough accuracy to determine the sign of CD exciton chirality.[9] The CD spectrum of gomadalactone B (**2**) shows a mirror CD image of (**1**) (Fig. 3),[7] hence the absolute stereochemistry of bicyclo moieties of (**1**) and (**2**) were opposite from each other. Gomadalactone C (**3**) has non-conjugated carbonyl groups in the bicyclo moiety and showed positive Cotton effect arising from carbonyl $n \rightarrow \pi^*$ transition at 290–350 nm region (Fig. 3). From the above, Figure 2 shows the relative structures and the steric relationship of compounds **1**–**3**, with the same absolute configuration at 4-position, but we did not hazard a guess to present tentative absolute configurations from the limited information of chirality here.

Gomadalactones were the only chiral group in the cocktail of several components with the contact pheromone activity. They had the same absolute configuration at the specific chiral center, arising from the common precursor biosynthesized in the insect. Aiming to determine their absolute stereochemistry and clarify the relationship between pheromone activity and chirality, synthetic studies are now in progress.

Acknowledgments

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5. Spectral data for (1*S**,4*R**,5*S**)-5-hydroxy-4-[(*E*)-7-hydroxy-4-methylhept-3-enyl]-4,8-dimethyl-3-oxabicyclo[3.3.0]octan-7-en-2,6-dione; Gomadalactone A (**1**): Colorless amorphous. High resolution FTICR-MS; *m*/*z* 331.1516 $[M+Na]^+$ (calcd for $C_{17}H_{24}O_5Na$ 331.1516, +ESI mode) and *m*/*z* 307.1552 $[M-H]^-$ (calcd for $C_{17}H_{23}O_5$ 307.1551, −ESI mode). UV and CD spectra were recorded in methanol with the same concentration (Fig. 3). UV (methanol, 1 mm cell), λ_{sh} 240 nm (abs 0.84), λ_{max} 222 nm (abs 0.99). CD (methanol, 1 mm cell), λ_{ext} 319.4 nm (θ +1.5 mdeg), λ_{ext} 279.6 nm (θ −0.1 mdeg), λ_{ext} 242.8 nm (θ +83.4 mdeg), λ 232.4 nm (θ ±0 mdeg), λ_{ext} 219.2 nm (θ −106.5 mdeg), λ 210.1 nm (θ ±0 mdeg). NMR assignments are shown in Table 1.
6. Spectral data for (1*R**,4*R**,5*R**)-5-hydroxy-4-[(*E*)-7-hydroxy-4-methylhept-3-enyl]-4,8-dimethyl-3-oxabicyclo[3.3.0]-octan-7-en-2,6-dione; Gomadalactone B (**2**): Colorless amorphous. High resolution FTICR-MS; *m*/*z* 331.1518 $[M+Na]^+$ (calcd for $C_{17}H_{24}O_5Na$ 331.1516, +ESI mode) and *m*/*z* 307.1553 $[M-H]^-$ (calcd for $C_{17}H_{23}O_5$ 307.1551, −ESI mode). UV and CD spectra were recorded in methanol with the same concentration (Fig. 3). UV (methanol, 1 mm cell), λ_{sh} 240 nm (abs 0.52), λ_{max} 220 nm (abs 0.71). CD (methanol, 1 mm cell), λ_{ext} 330 nm (θ

−0.7 mdeg), λ_{ext} 280 nm (θ −0.1 mdeg), λ_{ext} 242.8 nm (θ −52.0 mdeg), λ 231.6 nm (θ ±0), λ_{ext} 219.2 nm (θ +49.2 mdeg), λ 210.3 nm (θ ±0). NMR assignments are shown in Table 1.

7. Spectral data for (1*S**,4*R**,5*S**,8*S**)-5-hydroxy-4-[(*E*)-7-hydroxy-4-methylhept-3-enyl]-4,8-dimethyl-3-oxabicyclo[3.3.0]-octan-2,6-dione; Gomadalactone C (**3**): Colorless amorphous. High resolution FTICR-MS *m*/*z* 333.1673 $[M+Na]^+$ (calcd for $C_{17}H_{26}O_5Na$ 333.1673, +ESI mode) and at *m*/*z* 309.1710 $[M-H]^-$ (calcd for $C_{17}H_{25}O_5$ 309.1707, −ESI mode). UV and CD spectra were recorded in methanol with the same concentration (Fig. 3). UV (methanol, 1 mm cell), no significant peak. CD (methanol, 1 mm cell), λ_{ext} 313.0 nm (θ +31.9 mdeg), λ 264.9 nm (θ ±0 mdeg), λ_{ext} 245.4 nm (θ −2.1 mdeg), λ 239.7 nm (θ ±0 mdeg), λ_{ext} 222.2 nm (θ +5.9 mdeg), λ_{ext} 211.8 nm (θ +1.5 mdeg). NMR assignments are shown in Table 2.
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