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Note

Synthesis of the Racemate of (*Z*)-*exo*-α-Bergamotenal, a Pheromone Component of the White-spotted Spined Bug, *Eysarcoris parvus* Uhler

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The racemate of (*Z*)-*exo*-α-bergamotenal, a sex pheromone component of the white-spotted spined bug, was synthesized from racemic *exo*-α-bergamotene by a five-step sequence involving regioselective epoxidation and (*Z*)-selective Wittig olefination reactions. The ^{1}H- and ^{13}C-NMR spectra of the synthetic sample were identical with those of the natural material.

Key words: bergamotenal; sesquiterpene; pheromone; white-spotted spined bug; *Eysarcoris parvus*

The white-spotted spined bug (*Eysarcoris parvus* Uhler) is a notorious pest to many agricultural crops, especially for rice production in Japan. A few years ago, we reported the presence of the male-specific sex pheromone of the stink bug consisting of three components,[1,2] and quite recently, the structure of one of these components was proposed to be (*Z*)-*exo*-α-bergamotenal (**1**) from analyses of its IR, MS, and NMR data (Leal, W. S., Men, H.-C., Kuwahara, S., Hasegawa, M., manuscript in preparation). Although this aldehyde (**1**) had been prepared for use in perfumery from (*Z*)-*exo*-α-bergamotenol (**8**) contained in sandalwood essential oil,[3,4] our literature survey revealed **1** to be a new naturally occurring compound. From the standpoint of chemical ecology, it is worth mentioning that structurally related *endo*-bergamotane-type sesquiterpenes (**9** and **10**) have been isolated from wild tomato leaves (*Lycopersicon hirsutum*) as components of the oviposition stimulant of the corn earthworm (*Heliothis zea*).[5-7] To the best of our knowledge, however, the isolation of **1** from the stink bug is the first example of obtaining bergamotane-type natural products from non-plant sources, except for one case, in which α-*trans*-bergamotol acetate was obtained as a volatile metabolite from Caribbean coral of the genus *Gorgonia*, although the geometry of the double bond was not specified.[8] This unique finding prompted us to embark on the synthesis of **1** to confirm the proposed structure and to supply a sufficient amount of the sample for biological studies. To begin with, we report in this note the synthesis of the racemate of **1**.

Known bicyclic ketone **3a**,[9,10] which had been prepared from farnesic acid chloride (**2**) *via* [2 + 2] cycloadditon of an intermediary vinylketene, was first treated with hydrazine in acetic acid to give the corresponding hydrazone (**3b**).[9] According to Corey's method,[9] this hydrazone (**3b**) was exposed to basic conditions (*tert*-BuOK, DMSO) to obtain $\Delta^{2,15}$-olefinic hydrocarbon **4a** (*exo*-β-bergamotene), which is known to be convertible into the corresponding $\Delta^{2,3}$-olefin (**4b**, *exo*-α-bergamotene) by treating with hydriodic acid in benzene.[11] To our surprise, however, this Wolff-Kishner reduction directly gave the thermodynamically more stable $\Delta^{2,3}$-product (**4b**) almost exclusively (**4a**:**4b** = *ca.* 1:27) instead of **4a** which had previously been obtained by Corey and Desai.[9] The double bond migration from the $\Delta^{2,15}$-position to the $\Delta^{2,3}$-position is considered to be ascribable to the reaction time and temperature applied, since **3b** was treated with potassium *tert*-butoxide in DMSO for 12 h at room temperature in the preceding experiment,[9] while in our case, the hydrazone (**3b**) was exposed to basic conditions for a longer period (30 h) at a higher temperature (65°C). In order to confirm this presumption, the reduction was repeated by using exactly the same conditions as those reported in the literature.[9] Under these condi-

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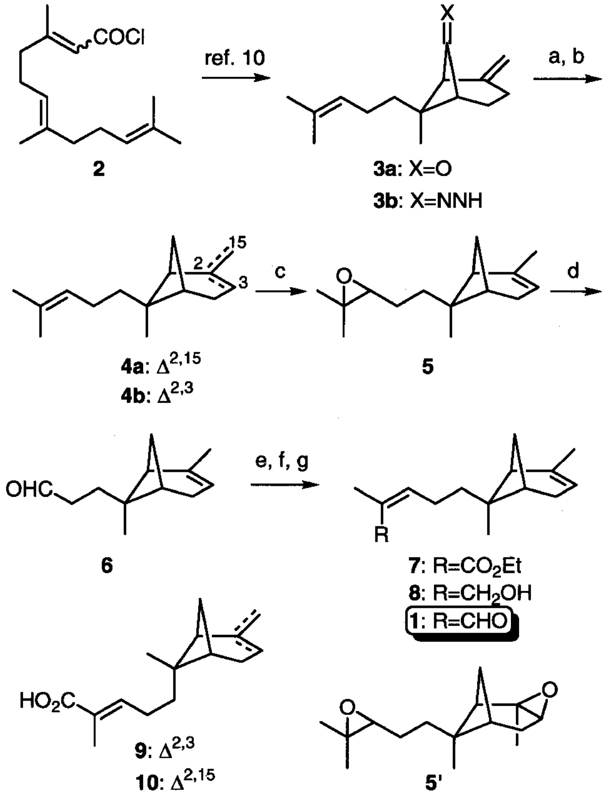

Figure. Reagents: a) N_2H_4, AcOH, EtOH; b) *t*-BuOK, DMSO; c) *m*-CPBA, aq. $NaHCO_3$, CH_2Cl_2; d) H_5IO_6, H_2O-THF; e) NaH, $(o\text{-Tolyl-O})_2P(O)CH(CH_3)CO_2Et$, THF; f) DIBAL, THF; g) MnO_2, hexane

tions, **4a** was indeed obtained as the major product (**4a**:**4b** = *ca.* 7:1). Furthermore, when the $\Delta^{2,15}$-olefinic compound (**4a**) was treated with *tert*-BuOK in DMSO at 60°C for 28 h, it was gradually transformed into **4b**, producing a 1:27 mixture of **4a** and **4b**. These results clearly show that the isomerization of the initially formed $\Delta^{2,15}$-olefinic reduction product (**4a**) into the $\Delta^{2,3}$-olefin (**4b**) was brought about during the Wolff-Kishner reduction by exposing **4a** to the prolonged reaction time and higher temperature under the strongly basic conditions. After chromatographic purification, the diene (**4b**) was subjected to an epoxidation reaction by using *m*-chloroperbenzoic acid. Fortunately, this oxidation proceeded regioselectively to give a mixture of **5** and bis-epoxidation product **5'** in a ratio of 6.6:1. This selectivity was probably due to steric hindrance around the $\Delta^{2,3}$-double bond of **4b**. The epoxide ring of **5** was cleaved with periodic acid to give aldehyde **6**, which was then exposed to (*Z*)-selective Wittig olefination conditions[12] to give **7** in an 83% yield after chromatographic purification. This ester (**7**) was reduced with diisobutylaluminum hydride to afford allylic alcohol **8**. Finally, oxidation of **8** with manganese dioxide completed the synthesis of $(\pm)$-**1**. The ^{1}H- and ^{13}C-NMR spectra of the synthetic sample were identical to those of the natural pheromone component. The synthesis of **1** in an optically active form is now underway to determine the absolute configuration of **1**.

Experimental

IR spectra were measured with a Jasco IR Report-100 spectrometer. ^{1}H-NMR spectra were recorded with a Varian Gemini 2000 (300 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard, unless otherwise stated. Mass spectra were recorded with a Jeol JMS-700 spectrometer. Merck silica gel 60 (70–230 mesh) was used for column chromatography.

(1R,5R*,6S*)-2,6-Dimethyl-6-(4-methyl-3-pentenyl)bicyclo[3.1.1]hept-2-ene (4b).* To a stirred solution of **3a** (1.41 g, 6.47 mmol) and acetic acid (0.55 ml, 9.61 mmol) in absolute ethanol (97 ml) was added anhydrous hydrazine (1.24 g, 38.7 mmol), and the mixture was stirred at 30°C for 48 h. The mixture was then diluted with ether (300 ml), and the resulting ethereal solution was successively washed with 1 M NaOH aq. and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 1.70 g of crude **3b** as a yellow oil; IR ν_{max} cm^{-1}: 3350 (m), 3070 (w), 1690 (m), 1640 (m). As described in the text, compound **3b** was converted into a 1:27 mixture of **4a** and **4b** in a 42% yield by treating with potassium *tert*-butoxide in DMSO for 30 h at 65. However, by raising the reaction temperature to 85°C, the reaction time could be shortened to 15 h, and the chemical yield of **4b** was improved to 52%, while the ratio of **4a** and **4b** (1:27) was maintained, as shown in the following description. Crude hydrazone **3b** (1.70 g) was dissolved in DMSO (64 ml), and potassium *tert*-butoxide (7.89 g, 70.3 mmol) was added to the solution. The mixture was stirred at 85°C for 15 h, and then diluted with pentane (400 ml). The pentane solution was successively washed with 1 M HCl aq. and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue (0.76 g) was chromatographed over silica gel (58 g, eluted with hexane) to give 0.680 g (52%) of **4b** and 0.025 g (2%) of **4a**. **4b**: $R_f = 0.78$ [Merck silica gel 60 F_{254} (No. 5715), developed with hexane]; IR ν_{max} cm^{-1}: 3020 (w), 2920 (s), 1465 (m), 1375 (m), 1215 (w), 1120 (w), 1085 (w), 1015 (w), 890 (w), 790 (m); ^{1}H-NMR δ: 0.83 (3H, s, 6-CH_3), 1.17 (1H, d, $J = 8.5$ Hz, 7-H), 1.58–1.74 (2H, m, $1'$-H), 1.63 (3H, br s, $4'$-CH_3), 1.66 (3H, q, $J = 1.7$ Hz, 2-CH_3), 1.70 (3H, br s, $4'$-CH_3), 1.91–2.06 (3H, m), 2.08–2.19 (2H, m), 2.20–2.30 (1H, m, 4-H), 2.32 (1H, dt, $J =$ 8.5, 5.8 Hz, 7-H), 5.17 (1H, tm, $J = 7.1$ Hz, $3'$-H), 5.18–5.23 (1H, m, 3-H); HREIMS m/z (M^+): calcd. for $C_{15}H_{24}$, 204.1878; found, 204.1881. The ^{1}H-NMR spectral data of **4b** were identical with those reported in the literature.[11] **4a**: $R_f = 0.69$ [Merck silica gel 60 F_{254} (No. 5715), developed with hexane]; IR ν_{max} cm^{-1}: 3070 (w), 2950 (s), 2925 (s), 2850 (s), 1640 (w),

1460 (m), 1380 (m), 880 (w); ^{1}H-NMR δ: 0.71 (3H, s, 6-CH$_3$), 1.42 (1H, d, J = 9.9 Hz, 7-H), 1.54–1.68 (2H, m), 1.62 (3H, 4′-CH$_3$), 1.70 (3H, s, 4′-CH$_3$), 1.78–1.86 (2H, m), 1.89–2.09 (3H, m), 2.20–2.35 (2H, m), 2.46–2.63 (2H, m), 4.56 (1H, br s, 2-methylene), 4.62–4.64 (1H, m, 2-methylene), 5.16 (1H, tm, J = 7.4 Hz, 3′-H). The ^{1}H-NMR spectral data of **4a** were identical with those reported in the literature.[9]

Isomerization of 4a into 4b. A mixture of **4a** (16.0 mg, 0.0784 mmol) and potassium *tert*-butoxide (48.0 mg, 0.428 mmol) in DMSO (1 ml) was stirred at 60°C for 28 h. The mixture was diluted with hexane and successively washed with 1 M HCl aq. and brine. The organic layer was dried (MgSO$_4$) and concentrated *in vacuo* to give an oil (10 mg), whose ^{1}H-NMR analysis revealed that the crude product was a 27:1 mixture of **4b** and **4a**.

(1R,5R*,6S*)-2,6-Dimethyl-6-(4-methyl-3,4-epoxypentyl)bicyclo[3.1.1]hept-2-ene (5)*. To a stirred mixture of **4b** (550 mg, 2.70 mmol), 0.5 M NaHCO$_3$ aq. (19.5 ml, 9.75 mmol) and dichloromethane (24 ml) was added a solution of *m*-chloroperbenzoic acid (65%, 720 mg, 2.71 mmol) in dichloromethane (32 ml) over 2 h at 0°C. After 4 h, the mixture was successively washed with 1 M NaOH aq. and water, dried (Na$_2$SO$_4$) and concentrated *in vacuo*. The residue (0.73 g) was chromatographed over silica gel (30 g, hexane-ethyl acetate, 9:1) to give 510 mg (86%) of **5** along with 80 mg (13%) of **5′**. **5**: IR $\nu_{\max}$ cm^{-1}: 2955 (s), 2920 (s), 2875 (m), 1445 (m), 1375 (s), 1320 (w), 1245 (w), 1215 (w), 1120 (m), 1095 (w), 870 (w), 790 (w); ^{1}H-NMR δ: 0.82 (3H, s, 6-CH$_3$), 1.19 (1H, d, J = 8.5 Hz, 7-H), 1.29 (3H, s, 4′-CH$_3$), 1.32 (3H, s, 4′-CH$_3$), 1.62–1.74 (2H, m, 1′-H), 1.65 (3H, q, J = 1.9 Hz, 2-CH$_3$), 1.88–2.06 (3H, m), 2.08–2.18 (2H, m), 2.20–2.32 (1H, m, 4-H), 2.32 (1H, dt, J = 8.5, 5.8 Hz, 7-H), 2.74 (1H, t, J = 6.2 Hz, 3′-H), 5.21 (1H, br s, 3-H); HREIMS m/z (M$^+$): calcd. for $C_{15}H_{24}O$, 220.1827; found, 220.1828. **5′**: IR $\nu_{\max}$ cm^{-1}: 2950 (s), 2920 (s), 2870 (m), 1440 (m), 1375 (s), 1320 (w), 1245 (w), 1120 (m), 1090 (w), 870 (w), 790 (w); ^{1}H-NMR δ: 0.92 (3H, s, 6-CH$_3$), 1.28 (3H, d, J = 1.4 Hz, 2-CH$_3$), 1.32 (3H, s, 4′-CH$_3$), 1.33 (3H, s, 4′-CH$_3$), 1.42–1.76 (4H, m), 1.76–1.89 (2H, m), 1.89–2.07 (2H, m), 2.73 (1H, t, J = 6.2 Hz, 3′-H), 3.08 (1H, br d, J = 4.0 Hz, 3-H); HREIMS m/z (M$^+$): calcd. for $C_{15}H_{24}O_2$, 236.1776; found, 236.1775.

3-[(1R,5R*,6S*)-2,6-Dimethylbicyclo[3.1.1]hept-2-en-6-yl]propanal (6)*. To a stirred solution of **5** (520 mg, 2.36 mmol) in THF (3 ml) was added dropwise a solution of periodic acid (730 mg, 3.20 mmol) in water (1.9 ml) at 0°C. After 3 h, the mixture was poured into water and extracted with ether. The ethereal solution was successively washed with sat. NaHCO$_3$ aq. and brine, dried (MgSO$_4$) and concentrated *in vacuo*. The residue (0.48 g) was chromatographed over silica gel (30 g, hexane-ethyl acetate, 8:1) to give 340 mg (81%) of **6**. IR $\nu_{\max}$ cm^{-1}: 2960 (s), 2920 (s), 2880 (s), 2715 (w), 1725 (s), 1470 (w), 1445 (m), 1375 (m), 1260 (m), 1100 (m), 1025 (m), 805 (m); ^{1}H-NMR δ: 0.81 (3H, s, 6′-CH$_3$), 1.21 (1H, d, J = 8.8 Hz, 7′-H), 1.66 (3H, q, J = 1.8 Hz, 2′-CH$_3$), 1.89–2.01 (3H, m), 2.08–2.19 (2H, m), 2.22–2.33 (1H, m, 4′-H), 2.32 (1H, dt, J = 8.8, 5.5 Hz, 7′-H), 2.39–2.49 (2H, m), 5.22 (1H, br s, 3′-H), 9.84 (1H, t, J = 1.9 Hz, CHO); HREIMS m/z (M$^+$): calcd. for $C_{12}H_{18}O$, 178.1358; found, 178.1355.

Ethyl (Z)-5-[(1R,5R*,6S*)-2,6-dimethylbicyclo[3.1.1]hept-2-en-6-yl]-2-methyl-2-pentenoate (7)*. To a stirred suspension of NaH (60% in mineral oil, 77.3 mg, 1.93 mmol, washed 3 times with hexane under argon) in THF (5 ml) was added a solution of ethyl 2-(di-*o*-tolylphosphono)propionate (500 mg, 1.44 mmol) in THF (5 ml) at 0°C, and the mixture was stirred at 15°C for 15 min. To this mixture was added dropwise a solution of **6** (220 mg, 1.23 mmol) in THF (7 ml) at −78°C. The mixture was stirred at the same temperature for 30 min, and then allowed to warm gradually to 0°C over 2 h. The mixture was poured into sat. NH$_4$Cl aq. and extracted with ethyl acetate. The organic layer was successively washed with water and brine, dried (MgSO$_4$) and concentrated *in vacuo*. The residue was chromatographed over silica gel (15 g, hexane-ethyl acetate, 10:1) to give 270 mg (83%) of **7**. IR $\nu_{\max}$ cm^{-1}: 2975 (s), 2950 (s), 2920 (vs), 2875 (s), 1715 (vs), 1450 (m), 1370 (m), 1220 (s), 1180 (s), 1160 (m), 1105 (m), 1080 (w), 1030 (w); ^{1}H-NMR δ: 0.84 (3H, s, 6′-CH$_3$), 1.18 (1H, d, J = 8.5 Hz, 7′-H), 1.30 (3H, t, J = 7.1 Hz, O-C-CH$_3$), 1.65 (3H, q, J = 1.6 Hz, 2′-H), 1.65–1.75 (2H, m, 5-H$_2$), 1.90 (3H, d, J = 1.1 Hz, 2-CH$_3$), 2.01 (1H, br t, J = 5.6 Hz, 1′-H), 2.08–2.18 (2H, m), 2.20–2.32 (1H, m), 2.32 (1H, dt, J = 8.5, 5.6 Hz, 7′-H), 2.40–2.52 (2H, m), 4.21 (2H, q, J = 7.1 Hz, O-CH$_2$), 5.18–5.23 (1H, m, 3′-H), 5.98 (1H, tq, J = 7.4, 1.1 Hz, 3-H); HREIMS m/z (M$^+$): calcd. for $C_{17}H_{26}O_2$, 262.1933; found, 262.1935.

(Z)-5-[(1R,5R*,6S*)-2,6-Dimethylbicyclo[3.1.1]hept-2-en-6-yl]-2-methyl-2-penten-1-ol (8)*. To a stirred solution of **7** (62.1 mg, 0.237 mmol) in THF (5 ml) was added dropwise a 1 M solution of diisobutylaluminium hydride in hexane (1.3 ml, 1.3 mmol) at −78°C. After 4 h, the reaction mixture was quenched with water (1.3 ml) and filtered through a Celite pad. The filtrate was dried over MgSO$_4$ and concentrated *in vacuo*. The residue (66.3 mg) was chromatographed over silica gel (30 g, hexane-ethyl acetate, 10:1) to give 52.0 mg (99.7%) of **8**. IR $\nu_{\max}$ cm^{-1}: 3310 (m), 3010 (w), 2950 (s), 2910

(s), 2870 (s), 1440 (m), 1370 (m), 1260 (m), 1090 (m), 1015 (s), 800 (m), 785 (m); ^{1}H-NMR δ: 0.83 (3H, s, 6′-CH$_3$), 1.18 (1H, d, $J=8.5$ Hz, 7′-H), 1.56 (1H, br s, OH), 1.58–1.71 (2H, m, 5-H$_2$), 1.65 (3H, q, $J=1.9$ Hz, 2′-CH$_3$), 1.81 (3H, d, $J=1.4$ Hz, 2-CH$_3$), 1.96–2.18 (5H, m), 2.21–2.30 (1H, m, 4′-H), 2.30 (1H, dt, $J=8.5$, 5.7 Hz, 7′-H), 4.16 (2H, br s, 1-H$_2$), 5.19–5.23 (1H, m, 3′-H), 5.36 (1H, br t, $J=7.6$ Hz, 3-H); HREIMS m/z (M$^+$): calcd. for $C_{15}H_{24}O$, 220.1827; found, 220.1833.

(Z)-5-[(1R,5R*,6S*)-2,6-Dimethylbicyclo[3.1.1]hept-2-en-6-yl]-2-methyl-2-pentenal (1).* A mixture of **8** (38.0 mg, 0.173 mmol) and manganese dioxide (chemically treated, purchased from Wako Pure Chemical Industries, 0.31 g, 3.6 mmol) in dry hexane (7 ml) was stirred at 0°C for 24 h. The mixture was filtered through a Celite pad, and the filtrate was concentrated *in vacuo*. The residue (49 mg) was chromatographed over silica gel (18 g, hexane-ethyl acetate, 10:1) to give 37.4 mg (99%) of **1**. IR ν_{max} cm^{-1}: 3015 (w), 2945 (s), 2910 (s), 2870 (s), 2720 (w), 1675 (vs), 1635 (w), 1440 (m), 1370 (m), 1340 (w), 1260 (m), 1080 (m), 1015 (m), 800 (m); ^{1}H-NMR (C_6D_6) δ: 0.76 (3H, s, 6′-H), 1.24 (1H, d, $J=8.8$ Hz, 7′-H), 1.40–1.48 (2H, m, 5-H$_2$), 1.64 (3H, q, $J=2.0$ Hz, 2′-H), 1.76 (3H, d, $J=1.4$ Hz, 2-CH$_3$), 1.86 (1H, dt, $J=1.3$, 5.6 Hz, 1′-H), 1.92–1.99 (1H, m, 5′-H), 2.01–2.28 (5H, m, 4-H$_2$, 4′-H$_2$, 7′-H), 5.20–5.26 (1H, m, 3′-H), 6.00 (1H, dt, $J=1.4$, 8.2 Hz, 3-H), 10.12 (1H, s, CHO); ^{13}C-NMR (C_6D_6) δ: 16.5, 17.2, 22.4, 22.9, 31.3, 31.6, 38.7, 39.0, 41.2, 45.4, 117.0, 135.9, 144.2, 148.6, 189.9. The ^{1}H- and ^{13}C-NMR spectra of the synthetic material were identical with those of the natural pheromone component. The following data are for the ^{1}H-NMR spectra of **1** in other solvents. ^{1}H-NMR (CDCl$_3$) δ: 0.87 (3H, s, 6′-CH$_3$), 1.22 (1H, d, $J=8.8$ Hz, 7′-H), 1.66 (3H, q, $J=1.6$ Hz, 2′-CH$_3$), 1.74–1.82 (2H, m, 5-H$_2$), 1.78 (3H, br s, 2-CH$_3$), 2.01 (1H, br t, $J=5.5$ Hz, 1′-H), 2.10–2.20 (2H, m), 2.22–2.35 (2H, m), 2.50–2.64 (2H, m), 5.23 (1H, br s, 3′-H), 6.59 (1H, t, $J=8.0$ Hz, 3-H), 10.19 (1H, s, CHO); ^{1}H-NMR (CCl$_4$) δ: 0.87 (3H, s, 6′-CH$_3$), 1.22 (1H, d, $J=8.8$ Hz, 7′-H), 1.67 (3H, br s, 2′-CH$_3$), 1.73–1.84 (2H, m, 5-H$_2$), 1.75 (3H, br s, 2-CH$_3$), 2.00 (1H, br t, $J=5.8$ Hz, 1′-H), 2.10–2.23 (2H, m), 2.23–2.38 (2H, m), 2.51–2.66 (2H, m), 5.20 (1H, br s, 3′-H), 6.46 (1H, t, $J=8.2$ Hz, 3-H), 10.13 (1H, s, CHO); HREIMS m/z (M$^+$): calcd. for $C_{15}H_{22}O$, 218.1670; found, 218.1675. The ^{1}H-NMR spectrum of **1** measured in CCl$_4$ was identical with that reported in the literature.[3)]

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