チャイロコメノゴミムシダマシの性誘引フェロモン,4-メチル-1-ノナノールの絶対配置

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Original Article

Absolute Configuration of 4-Methyl-1-nonanol, a Sex Attractant of the Yellow Mealworm, *Tenebrio molitor* L.*

Yuichi TANAKA,** Hiroshi HONDA, Kanju OHSAWA*** and Izuru YAMAMOTO

Laboratory of Pesticide and Bio-organic Chemistry,
****Nodai Research Institute,*
Tokyo University of Agriculture, Setagaya-ku, Tokyo 156, Japan

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In an attempt to determine the absolute configuration of 4-methyl-1-nonanol, a sex attractant of the yellow mealworm, *Tenebrio molitor* L., both enantiomers were synthesized. The enantiomers and the natural attractant were converted to diastereomeric derivatives. The pheromonal activity of both enantiomers and the retention times of the derivatives on HPLC were compared with those of the natural attractant and its derivatives. The natural attractant was found (*R*)-(+)-4-methyl-1-nonanol.

INTRODUCTION

We have reported that 4-methyl-1-nonanol, which has an asymmetric carbon atom at the 4th position, is a sex attractant of the yellow mealworm, *Tenebrio molitor* L.[1] We here report its absolute configuration based on biological and chemical evidences.

MATERIALS AND METHODS

1. *Bioassay*

The (*R*)-, (*S*)-, the racemic and the natural 4-methyl-1-nonanols were compared in terms of pheromonal activity. Sex attractancy was determined by the same bioassay method as described in the previous paper.[1] When the compounds were given at lower doses of about 10 ng of sex attractant, males were attracted to the where a sample was, but when they were given higher doses (corresponding to more than 20 ng), males mounted on other males and attempted a copulation with their genital organs extruding due to a synergistic interaction[1] between the cuticular lipids[2] on a male and a sex attractant.

The pheromonal activity was judged according to the following scale: —, among 20 males, less than 15 were attracted to a sample; +, more than 15 were attracted to the sample; ++, more than five males mounted on other males and attempted a copulation.

2. *Instruments*

IR spectra were taken in liquid film on a Shimadzu IR-27S. NMR spectra were recorded in $CDCl_3$ solutions at 60 MHz with 1% TMS as an internal standard on a JEOL JNM-PMX 60 spectrometer. EI-MS analyses were performed on a Shimadzu Auto GC-MS 6020 at 20 eV. Optical rotations were measured on a JASCO DIP-140 digital polarimeter.

3. *General Procedures for the Synthesis*

As shown in Fig. 1, both enantiomeric 4-methyl-1-nonanols were synthesized from (*R*)-

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** Present address: S. T. Chemical Co., Ltd., Shinjuku-ku, Tokyo 161, Japan.

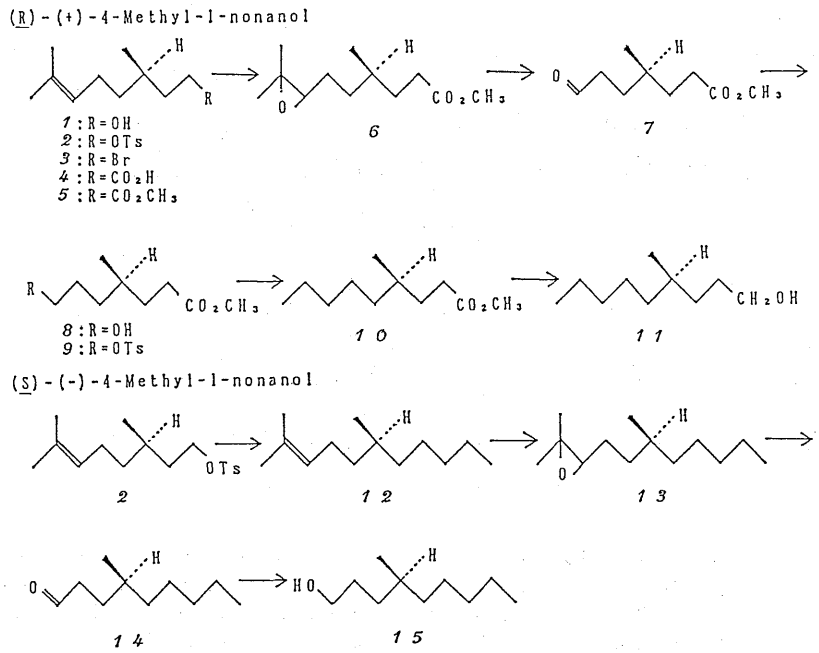

Fig. 1 Synthesis of enantiomeric 4-methyl-1-nonanols.

(+)-citronellol **1**, $[\alpha]_D^{22}$+5.52° (neat); lit.[3] $[\alpha]_D^{25}$+5.51° (neat), which had been derived from optically pure (*R*)-(+)-puregone,[3,4] $[\alpha]_D^{22}$+22.00° (neat); lit.[5] $[\alpha]_D^{24}$+23.18° (neat), *via* (*R*)-(+)-citronellic acid, $[\alpha]_D^{22}$+8.68° (neat); $[\alpha]_D^{22}$+10.11° (*c*=2.94, $CHCl_3$); lit.[3] $[\alpha]_D^{25}$ +8.72° (neat); lit.[3] $[\alpha]_D^{25}$+10.2° (*c*=2.48, $CHCl_3$).

Tosylate **2** prepared from alcohol **1** was treated with lithium bromide to give bromide **3**. Grignard reaction of **3** to carbon dioxide gave acid **4**, which was methylated with methanol and conc. sulfuric acid to give ester **5**. Epoxydation of **5** with *m*-chloroperbenzoic acid (*m*-CPBA) yielded epoxide **6**, which was cleaved with periodic acid to aldehyde **7**, and this was reduced with sodium borohydride to give alcohol **8**. The chain of **8** was elongated by treating tosylate **9** with $(C_2H_5)_2CuLi$[6] to give ester **10**. The reduction of **10** with lithium aluminum hydride produced (*R*)-(+)-4-methyl-1-nonanol [(*R*)-form] **11**.

To synthesize an (*S*)-enantiomer the following steps were taken: Tosylate **2** was coupled with propylmagnesium bromide in the presence of Li_2CuCl_4[7] to give olefin **12**. Epoxydation of **12** with *m*-CPBA yielded epoxide **13**, which was cleaved with a periodic acid to aldehyde **14**. The reduction of aldehyde **14** with lithium aluminum hydride produced (*S*)-(—)-4-methyl-1-nonanol [(*S*)-form] **15**.

3.1 (*R*)-(+)-*4-Methyl-1-nonanol*

(*R*)-(—)-*1-Bromo-3,7-dimethyl-6-octene* **3**: *p*-Toluenesulfonyl chloride (76 g) was added to a stirred and ice-cooled solution of **1** (54.5 g) in dry pyridine (160 ml) for 3 hr. After stirring at room temperature for 1 hr, the mixture was poured into water and extracted with ether. The extract was washed with 5% aq. HCl and sat. $NaHCO_3$, and dried over $MgSO_4$. After evaporation, crude tosylate **2** (95 g) thus obtained was used for the next step without further purification. Lithium bromide (55 g) was added to a solution of **2** (95 g) in acetone (1000 ml), and refluxed for 1 hr. After the solvent was evaporated, the residue was poured into water, extracted with ether and dried over $MgSO_4$. The residue was evaporated, and distilled *in vacuo* to give **3** (58.3 g, 76%), bp 75–76°C (3 mmHg); $[\alpha]_D^{22}$—6.56° (neat); MS *m/z*: 55, 56, 57, 69 as a base peak,

83, 97, 111, 139, 162, 164, 218, 220 (M^+); lit.[8] $[\alpha]_D^{20}$ −6.93° (neat).

(R)-(−)-4,8-Dimethyl-7-nonenoic acid **4**: A solution of **3** (58.3 g) in ether (150 ml) was added to a stirred and refluxed suspension of Mg (6.5 g) in dry ether (350 ml), and the mixture was stirred at the same temperature for 2 hr. The mixture was cooled to 0°C, and stirred under carbon dioxide gas for more than 12 hr. The mixture was poured into sat. NH_4Cl and extracted with ether. From the ether solution, an acidic compound was extracted with 5% aq. NaOH. After neutralization, the acid was shaken with ether, washed with water, and dried over Na_2SO_4. The ether extract was evaporated, and the residue distilled *in vacuo* to give **4** (25 g, 50%), bp 132–134°C (4 mmHg); $[\alpha]_D^{22}$ −3.85° (neat); IR ν_{max}^{film} cm^{-1}: 2930 (s), 2700 (w), 1710 (s), 1450 (m), 1420 (m), 1380 (m), 1290 (m), 1220 (m), 945 (m), 835 (w); lit.[9] $[\alpha]_D^{22}$ −3.64° (neat).

Methyl (R)-(−)-4,8-dimethyl-7-nonenoate **5**: Conc. H_2SO_4 (5 ml) was added to a solution of **4** (25 g) in methanol (100 ml), and the water was removed with benzene azeotropically. After ether was added, the mixture was washed with water, 5% aq. NaOH and sat. NaCl, and dried over Na_2SO_4. After the solvent was evaporated, the residue was distilled *in vacuo* to give **5** (23 g, 85%), bp 88–90°C (3 mmHg); $[\alpha]_D^{22}$ −0.95° (neat); IR ν_{max}^{film} cm^{-1}; 2960 (s), 2940 (s), 2870 (m), 1750 (s), 1440 (m), 1380 (m), 1260 (m), 1200 (m), 1175 (s), 1115 (m), 1100 (m), 1025 (w), 1000 (w), 840 (w); MS *m/z*: 69 as a base peak, 110, 151, 166, 198 (M^+); lit.[9] $[\alpha]_D^{22}$ −0.98° (neat).

Methyl (4R)-(−)-7,8-epoxy-4,8-dimethylnonanoate **6**: An ice-cooled solution of *m*-CPBA (85% purity, 26 g) in dry CH_2Cl_2 (300 ml) was added to an ice-cooled solution of **5** (26 g) in dry CH_2Cl_2 (200 ml). The mixture was left to stand for 8 hr at 10°C, and then filtered. The filtrate was washed with sat. Na_2CO_3 and water, and dried over Na_2SO_4. The solvent was evaporated, and the residue distilled *in vacuo* to give **6** (19 g, 90%), bp 108–115°C (5 mmHg); $[\alpha]_D^{22}$ −0.13° (neat); IR ν_{max}^{film} cm^{-1}: 2970 (s), 2720 (m), 1750 (s), 1460 (m), 1440 (m), 1385 (m), 1260 (m), 1200 (m), 1175 (m), 1125 (m), 1025 (w), 1000 (w), 880 (m), 800 (w); ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 0.90 (3H, d, J=6 Hz), 1.24 (3H, s), 1.27 (3H, s), 2.30 (2H, t, J=6 Hz), 2.65 (1H, t, J=6 Hz), 3.62 (3H, s); lit.[9] $[\alpha]_D^{19}$ −0.12° (±0.02, neat).

Methyl (R)-(−)-7-oxo-4-methylheptanoate **7**: A solution of a periodic acid ($HIO_4 \cdot 2H_2O$, 25 g) in THF (130 ml) was added dropwise to a stirred solution of **6** (18 g) in ether (130 ml) for 30 min. After stirred for 2 hr, the mixture was poured into 5% aq. $NaHCO_3$ and shaken with ether. The extract was washed with water, and the ether evaporated, and the residue purified by GC to give **7** (6.8 g, 43%); $[\alpha]_D^{26}$ −1.51° (c=2.72, $CHCl_3$); IR ν_{max}^{film} cm^{-1}: 2960 (s), 2900 (m), 2760 (w), 1750 (s), 1440 (m), 1385 (w), 1265 (m) 1200 (m), 1170 (m), 1105 (m), 1020 (w), 1000 (m), 900 (w), 855 (w), 765 (w); ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 0.88 (3H, d, J= 6 Hz), 1.1–1.9 (5H, m), 2.0–2.5 (4H, m), 3.55 (3H, s), 9.65 (1H, t, J=2 Hz); lit.[9] $[\alpha]_D^{22}$ −0.71° (±0.02, neat).

Methyl (R)-(−)-7-hydroxy-4-methylheptanoate **8**: Sodium borohydride (3 g) was added to a stirred and ice-cooled solution of **7** (6.8 g) in methanol (100 ml) for 1 hr. The mixture was adjusted to pH 4 with acetic acid, poured into water, and shaken with ether. The ether solution was washed with sat. $NaHCO_3$ and sat. NaCl, and dried over $MgSO_4$. The ether was evaporated, and the residue passed through Florisil, and distilled *in vacuo* to give **8** (3.4 g, 50%), $[\alpha]_D^{26}$ −0.66° (c=2.72, $CHCl_3$); IR ν_{max}^{film} cm^{-1}: 3360 (s), 2950 (s), 2900 (s), 1750 (s), 1440 (s), 1380 (m), 1340 (m), 1270 (m), 1200 (m), 1175 (m), 1110 (m), 1065 (m), 1020 (m), 900 (w); ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 0.80 (3H, d, J=6 Hz), 1.1–1.8 (8H, br), 2.30 (2H, t, J= 6 Hz), 3.4–3.7 (5H, m); lit.[9] $[\alpha]_D^{21}$ −0.98° (±0.02, neat).

Methyl (R)-(−)-4-methylnonanoate **10**: Lithium (1.7 g) was added to a stirred and cooled dry ether (40 ml) at −30°C under nitrogen. To the mixture, a solution of bromoethane (11 g) in dry ether (30 ml) was added for 30 min, and stirred for 30 min to give ethyllithium solution in ether (35 ml). The solution was then added to a suspension of copper (I) iodide (CuI, 3.8 g) at −30°C in ether (10 ml) for 10 min. The mixture was stirred for 30 min, and to this mixture a solution of tosylate **9** (4 g) prepared from **8** (3 g) in ether (16 ml) was added, and stirred for 30

min. The mixture was poured into sat. NH_4Cl, and extracted with ether. The ether extract was washed with sat. NaCl and water, and dried over Na_2SO_4. After the ether was evaporated, the residue was passed through Florisil, and distilled *in vacuo* to give ester **10** (0.5 g, 35%) bp 75–76°C (3 mmHg); $[\alpha]_D^{26}$ −0.24° (c=4.54, $CHCl_3$); IR ν_{max}^{film} cm^{-1}: 2960 (s), 2860 (m), 1750 (s), 1460 (m), 1435 (m), 1380 (m), 1260 (m), 1200 (m), 1175 (s), 1115 (m), 1025 (w), 1000 (w), 850 (w), 765 (s); ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 0.71–1.10 (6H, m), 1.10–1.80 (11H, m), 2.28 (2H, t, J=6 Hz), 3.63 (3H, s); MS m/z: 74, 87 as a base peak, 113, 115, 129, 155 (M^+-CH_3O).

(R)-(+)-4-Methyl-1-nonanol **11**: A solution of **10** (0.5 g) in ether (5 ml) was added to a stirred suspension of lithium aluminum hydride (0.2 g) in ether (20 ml) for 10 min. The mixture was poured into water, and shaken with ether. Then the ether extract was washed with 5% aq. HCl and water, and dried over Na_2SO_4. After ether was evaporated, the residue was distilled *in vacuo* to give **11** [(*R*)-form] (0.4 g, 85%). $[\alpha]_D^{26}$+1.33° (c=2.55, $CHCl_3$); IR ν_{max}^{film} cm^{-1}: 3340 (s), 2940 (s), 2870 (s), 1460 (m), 1380 (m), 1130 (m), 1060 (m), 905 (w), 730 (w); ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 0.70–1.05 (6H, m), 1.05–1.80 (13H, br), 1.43 (1H, s), 3.56 (2H, t, J=6 Hz); MS m/z: 56, 57 as a base peak, 69, 84, 97, 112, 140 (M^+-H_2O).

3.2 (S)-(−)-4-Methyl-1-nonanol

(S)-(−)-2,6-Dimethyl-2-undecene **12**: A solution of propylmagnesium bromide in THF (200 ml) prepared from 1-bromopropane (8.6 g) and magnesium (2 g) was ice-cooled. To this a solution of **2** (20.5 g) in THF (70 ml) and then a solution of dilithium tetrachloro cuprate in THF (2.2 ml) prepared from lithium chloride (LiCl, 0.02 g) and copper (II) chloride ($CuCl_2$, 0.03 g) were added. The mixture was stirred for 20 hr, poured into sat. NH_4Cl, and shaken with ether. The ether extract was washed with water and dried over Na_2SO_4. The ether was evaporated, and the residue was distilled *in vacuo* to give **12** (5.4 g, 47%), bp 62–66°C (2 mmHg); $[\alpha]_D^{22}$−1.21° (neat); IR ν_{max}^{film} cm^{-1}: 2980 (s), 2950 (s), 2880 (s), 1465 (m), 1380 (m), 1120 (w), 1100 (w), 995 (w), 830 (w), 730 (w); ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 0.63–1.00 (6H, m), 1.00–1.55 (11H, br), 1.59 (3H, s), 1.66 (3H, s), 1.94 (2H, q, J=7 Hz), 5.06 (1H, t, J=7 Hz).

(6S)-(−)-2,3-Epoxy-2,6-dimethylundecane **13**: The compound **13** was prepared from **12** (4.4 g) in the same manner as described for the preparation of **6**. **13** (3.3 g, 69%); bp 71–72°C (3 mmHg); $[\alpha]_D^{22}$−0.24° (neat); IR ν_{max}^{film} cm^{-1}: 2980 (s), 2950 (s), 2880 (s), 1475 (m), 1385 (s), 1365 (w), 1260 (m), 1130 (m), 910 (w), 880 (m), 800 (w), 745 (w), 690 (w); ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 0.63–1.00 (6H, m), 1.00–1.80 (13H, m), 1.26 (3H, s), 1.30 (3H, s), 2.64 (1H, t, J= 6 Hz).

(S)-(−)-4-Methyl-1-nonanal **14**: The compound **14** was prepared from **13** (3 g) in the same manner as described for the preparation of **7**. **14** (1.8 g, 76%); bp 51–52°C (2 mmHg); $[\alpha]_D^{22}$−0.64° (neat); IR ν_{max}^{film} cm^{-1}: 2970 (s), 2940 (s), 2870 (s), 2750 (m), 1735 (s), 1465 (s), 1420 (m), 1395 (m), 1385 (m), 730 (w); ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 0.60–1.03 (6H, m), 1.03–1.82 (11H, br), 2.36 (2H, q, J=6 Hz), 9.66 (1H, t, J=2 Hz); MS m/z: 56, 57 as a base peak, 59, 112 (M^+-CH_2CHOH).

(S)-(−)-4-Methyl-1-nonanol **15**: The compound **15** was prepared from **14** (1.8 g) in the same manner as described for the preparation of **11**. **15** [(*S*)-form] (1.3 g, 71%); $[\alpha]_D^{22}$−1.87° (neat); $[\alpha]_D^{26}$−1.32° (c=2.43, $CHCl_3$). The IR and MS spectra were identical with those of **11**.

4. Analysis of Both Diastereomers of N-[(R)-1-Phenylethyl]-4-methyl-1-nonanamide by HPLC

4.1 Derivatization to diastereomers

The Jones reagent (1 ml) prepared from conc. H_2SO_4 (6 ml), chromic anhydride (6.7 g) and water (50 ml) was added to a solution of either enantiomeric 4-methyl-1-nonanol **11** or **15** (about 0.1 mg) in acetone (2 ml). After stirring for 20 hr, the solution was poured into water and extracted with pentane. From the pentane solution, an acidic compound was extracted with 5% aq. NaOH. After the extract neutralized, the acid was extracted with ether, washed with water, and dried over Na_2SO_4. After the ether was evaporated, the obtained (*R*)-4-methyl-1-nonanoic acid **11a** or (*S*)-4-methyl-1-nonanoic acid **15a** was used for the next step without further purification.

Oxalyl chloride (0.2 ml) was added to a solution of **11a** or **15a** (about 0.1 g) in dry benzene (5 ml). The solution was refluxed for 30 min, oxalyl chloride was removed by evaporation to give (*R*)-4-methyl-1-nonyl chloride **11b** or (*S*)-4-methyl-1-nonyl chloride **15b**, which was used for the next step without further purification.

A solution of (*R*)-(+)-1-phenylethylamine (0.1 g) in dry ether (3 ml) was added to an ice-cooled solution of **11b** or **15b** (about 0.1 g) in dry ether (5 ml). After stirred for 1 hr, the mixture was poured into water and shaken with ether. The ether solution was then washed with 5% aq. HCl, 5% aq. NaOH and water, and dried over Na_2SO_4. The ether was evaporated, and the residue purified by TLC to give N-[(*R*)-1-phenylethyl]-(R)-4-methyl-1-nonanamide **11c** [(*R*)-amide] or N-[(*R*)-1-phenylethyl]-(S)-4-methyl-1-nonanamide **15c** [(*S*)-amide], as shown in Fig. 2. The IR and MS spectra of both amides, **11c** and **15c**, were identical. IR ν_{max}^{film} cm^{-1}: 3280 (s), 3040 (m), 2950 (s), 2900 (s), 1955 (w), 1880 (w), 1810 (w), 1750 (w), 1640 (s), 1550 (s), 1455 (s), 1385 (m), 1140 (m), 1030 (m), 920 (w), 770 (m), 705 (s); MS *m/z*: 105, 120, 163 as a base peak, 176, 275 (M^+).

4.2 Analysis by HPLC

Amides **11c** and **15c** were injected into a 3.9 mm i.d. × 30 cm stainless steel column, filled with μ PORASIL obtained from Waters Associates, Inc. The mobile phase was 30% v/v chloroform in hexane, which was pumped at a flow rate of 2.0 ml/min. Effluents were monitored at 254 nm. (*R*)-Amide **11c** and (*S*)-amide **15c** were both detected at 11.5 min and 11.0 min, respectively. The enantiomeric excesses were determined 88.0% for (*R*)-amide and 93.5% for (*S*)-amide from the peak areas.

RESULTS AND DISCUSSION

Natural 4-methyl-1-nonanol was derivatized to carboxamide with the above procedure to give N-[(*R*)-1-phenylethyl]-4-methyl-1-nonanamide [natural amide], whose MS spectrum was identical with that of (*R*)-amide or (*S*)-amide. In HPLC analysis the natural amide had the same retention time as (*R*)-amide (*Rt* = 11.5 min). (*S*)-Amide (*Rt* = 11.0 min) was not detected at all. As shown in Table 1, the synthetic (*R*)-form showed the same level

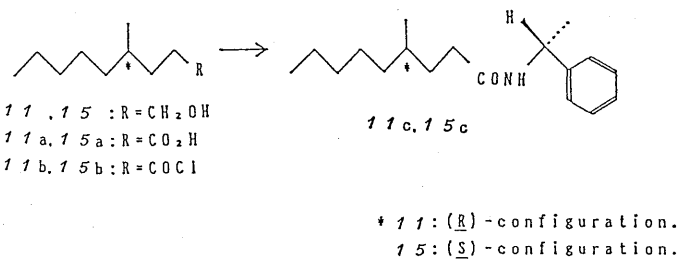

Fig. 2 Synthesis of N-[(*R*)-1-phenylethyl]-4-methyl-1-nonanamide derivatives.

Table 1 Comparison of (*R*), (*S*), racemic and natural 4-methyl-1-nonanols in pheromonal activity.

	Response at			
	2.5 ng	5 ng	10 ng	20 ng
Natural 4-methyl-1-nonanol	−	+	+	++
Racemic 4-methyl-1-nonanol	−	−	+	++
(*R*)-(+)-4-methyl-1-nonanol[a)]	−	+	+	++
(*S*)-(−)-4-methyl-1-nonanol[b)]	−	−	+	+

a) Enantiomeric excess was 88.0%.
b) Enantiomeric excess was 93.5%.

of pheromonal activity as the natural attractant. The natural attractant was therefore determined to be (*R*)-(+)-4-methyl-1-nonanol.

The synthetic (*S*)-form also showed some activity, although weak. A question is whether or not the (*S*)-form has an intrinsic activity, because the enantiomeric excess of the (*S*)-form was 93.5%. Supposing that half of the remaining 6.5% is (*R*)-form, then the (*R*)-form content in 10 ng of a (*S*)-form preparation is 0.325 ng, which is not a dose level high enough to induce any activity. We have, therefore, concluded that the (*S*)-form itself is active. The activity of racemate suggests that the (*S*)-form does not have any synergistic or antagonistic activity as the (*R*)-form.

There are three cases in the biological activity of pheromones that are chiral: 1) only one enantiomer has the activity, 2) both enantiomers have the same or quantitatively different activity, and 3) antagonism or synergism occurs between them.[10] A sex attractant of the yellow mealworm belongs to the second category, but there is only one enantiomer in the natural pheromone.

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要　　約

チャイロコメノゴミムシダマシの性誘引フェロモン，4-メチル-1-ノナノールの絶対配置

田中雄一，本田　博，大沢貫寿，山本　出

チャイロコメノゴミムシダマシの性誘引フェロモン，4-メチル-1-ノナノールの絶対配置を決定するため両鏡像異性体を合成した．そしてこれらの異性体ならびに天然性誘引フェロモンからジアステレオマー誘導体を得た．両鏡像異性体のフェロモン活性と誘導体のHPLCにおける保持時間を天然性誘引フェロモンのそれと比較し，天然性誘引フェロモンを(*R*)-(+)-4-メチル-1-ノナノールと決定した．