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Pheromone synthesis. Part 265: Synthesis and stereochemical composition of two pheromonal compounds of the female Korean apricot wasp, *Eurytoma maslovskii*☆

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ABSTRACT

2,10-Dimethyldodecyl propanoate and 2,8-dimethyldecyl propanoate are two pheromonal compounds secreted by the female Korean apricot wasp, *Eurytoma maslovskii*. The enantioselective synthesis of all the stereoisomers of both components was conducted; HPLC analysis based on the chiral derivatization method (Ohrui–Akasaka method) was applied for the clarification of the stereochemical composition of these two components. The most pheromonally active compound, (2*S*,10*R*)-dimethyldodecyl propanoate, was also the most abundant component in the cuticular extract.

1. Introduction

The wasp *Eurytoma maslovskii* (Hymenoptera: Eurytomidae) poses a serious threat to Korean apricot orchards. The cuticular extract of its females was shown to be active as a sex attractant, and then seven candidate structures, (*Z*)-15-methyl-7-nonacosene, (*Z*)-17-methyl-7-hentriacontene, 3,7-dimethylheptacosane, 3,7,11-trimethylnonacosane, 8,12-dimethyltriacontane, 8,18-dimethyltriacontane, and 3,7,17-trimethylnonacosane, were proposed for the pheromonal components on the basis of GC-MS analysis in 2016 [2]. The synthesis of all the seven pheromone candidates as stereoisomeric mixtures was previously reported by our group [2]. Even though the first four components (with unknown stereochemistry) were identified as part of the female-specific secretion of *E. maslovskii* via GC-MS analysis, various blend combinations of these components caught no males of *E. maslovskii* in field tests that were conducted in Korea between April and May in 2016. These results suggested that these hydrocarbons are not genuine pheromone [2]. In 2017, the synthesis of four tri-substituted pyrazines isolated from *E. maslovskii* was also reported [3]. Regrettably, these components also failed to attract male *E. maslovskii* in field test (conducted between April and May in 2017) despite showing strong electroantennogram activity [3]. Thus, in our continued efforts to clarify the structure of the genuine pheromone(s) of *E. maslovskii*, the components 2,10-dimethyldodecyl propanoate (**1**) and 2,8-dimethyldecyl propanoate (**2**) were reported as possible pheromone candidates (Fig. 1) [4]. The non-stereoselective and enantioselective synthesis of **1** and **2** enabled us to confirm the stereochemistry–activity relationship in these compounds as well as the total composition of the natural pheromone. The former was clarified via field bioassay that was executed in Korea [4], whereas the latter was determined using HPLC analysis based on a chiral derivatization method, namely the Ohrui–Akasaka method [5]. In

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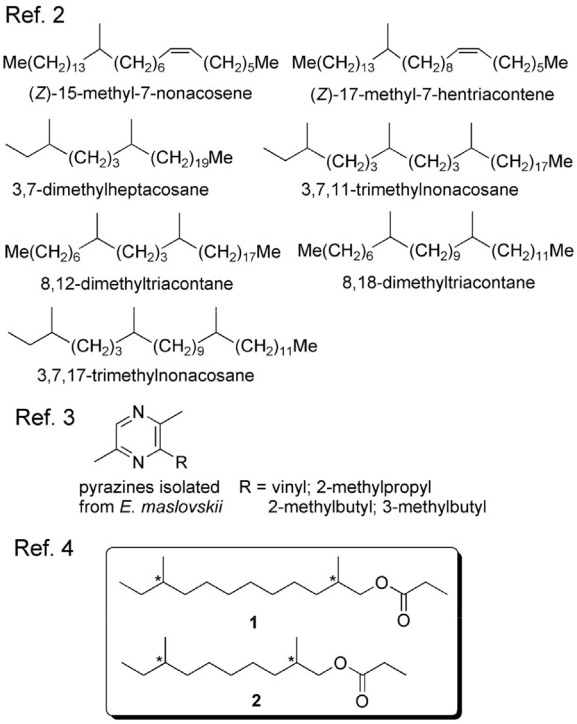


Fig. 1. Structures of *E. maslovskii* pheromone candidates.

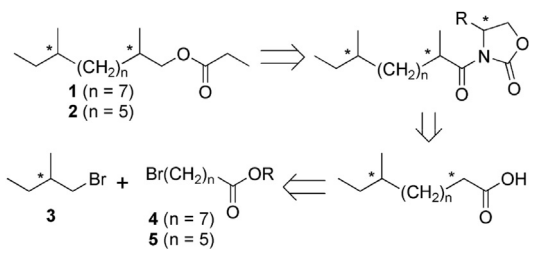
this paper, synthetic and analytical parts of studies on *E. maslovskii* pheromones are described in detail.

2. Results and discussion

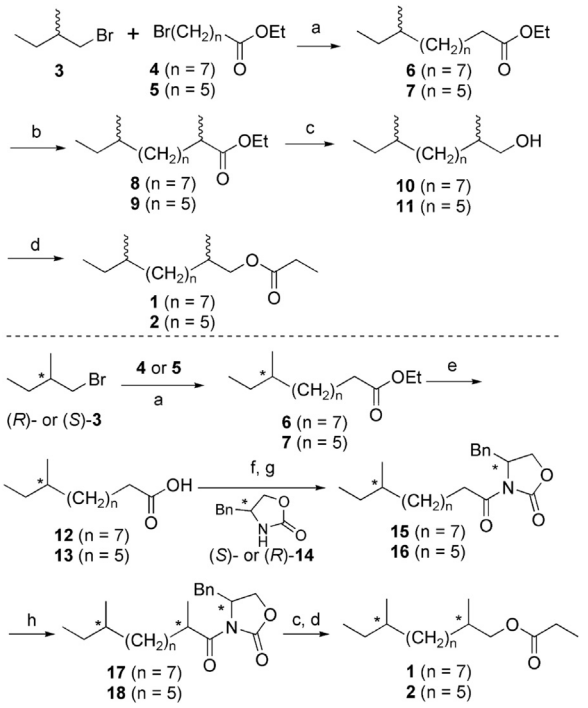
2.1. Synthesis of the pheromone candidates

The synthetic plan toward the candidate compounds **1** and **2** with high enantiomeric purity is shown in Scheme 1. The chiral center at C10 of **1** and C8 of **2** could be installed starting from optically active 1-bromo-2-methylbutane (**3**). The Grignard coupling between **3** and ω-bromoester (**4** or **5**) would be appropriate for elongation of carbon chain. Introduction of the chiral center at C2 of **1** and **2** would be possible by Evans' method [6], which is one of the most reliable and widely used method for conducting diastereoselective α-alkylation. The reductive cleavage of a chiral auxiliary followed by propanoylation would give the target compounds **1** and **2**.

As shown in Scheme 2, the non-stereoselective synthesis of **1** and **2** was first executed. According to the reported procedure [7], the Grignard coupling between **3** and ethyl 8-bromooctanoate (**4**) was mediated by CuBr to afford **6** (96%). Since diastereoselective methylation was unnecessary in this series, α-methylation of **6** was



Scheme 1. Synthetic plan.



Scheme 2. Synthesis of **1** and **2**.
Reagents: (a) Mg, THF; CuBr, NMP, THF; (b) LDA, MeI, HMPA, THF (c) $LiAlH_4$, THF; (d) EtCOCl, pyridine, CH_2Cl_2; (e) aq. NaOH, THF; (f) $(COCl)_2$; (g) **14**, *n*-BuLi, THF; (h) NaHMDS, MeI, THF.

performed by treatment with LDA and MeI to give **8** in 72% yield. Reduction of **8** with $LiAlH_4$ afforded **10** (93%), which was then esterified to furnish **1** as a mixture of all the possible stereoisomers (96%). In the same manner, a mixture of all the possible stereoisomers of **2** was also synthesized (41% from **3**) using ethyl 6-bromohexanoate (**5**) instead of **4**.

Since the MS profiles of the synthesized **1** and **2** were in good accordance with those of the naturally occurring pheromone candidates [4], we commenced with the synthesis of all the possible stereoisomers of **1** and **2**. The chiral starting material (*R*)-**3** was prepared according to the reported procedure from (*R*)-2-methylbutanoic acid [8], whereas (*S*)-**3** is commercially available. The Grignard coupling between (*S*)-**3** and **4** gave (*S*)-**6**, which was then hydrolyzed to afford (*S*)-**12**. After conversion of (*S*)-**12** into the corresponding acyl chloride, the product was treated with the lithium salt of (*S*)-**14** to give (4*S*,10′*S*)-**15** (63%, 4 steps). The diastereoselective methylation of (4*S*,10′*S*)-**15** was successfully achieved by treatment with NaHMDS and MeI to afford a mixture of (4*S*,2′*S*,10′*S*)- and (4*S*,2′*R*,10′*S*)-**17** (96:4). However, this mixture was easily separated by silica-gel column chromatography to give the pure (4*S*,2′*S*,10′*S*)-**17** (69%). After reductive cleavage of the chiral auxiliary (91%), the resulting (2*S*,10*S*)-**10** was then converted to (2*S*,10*S*)-**1** (83%). In the same manner, (2*R*,10*S*)-**1** was prepared by using (*R*)-**14** instead of (*S*)-**14**. By changing the starting bromide **3** from (*S*) to (*R*), (2*S*,10*R*)- and (2*R*,10*R*)-**1** were also prepared. All the possible stereoisomers of **2** were synthesized uneventfully.

All the synthesized **1** and **2** were then employed for the field bioassay. By the bioassay, (2*S*,10*R*)-**1** was shown to be the most active as the aggregation pheromone, whereas (2*S*,8*R*)-**2** and (2*S*,8*S*)-**2** were the second and third most active compounds, respectively [4]. All the synthesized intermediate alcohols (**10** and **11**) were used for analytical studies on the composition of the natural pheromone (*vide infra*).

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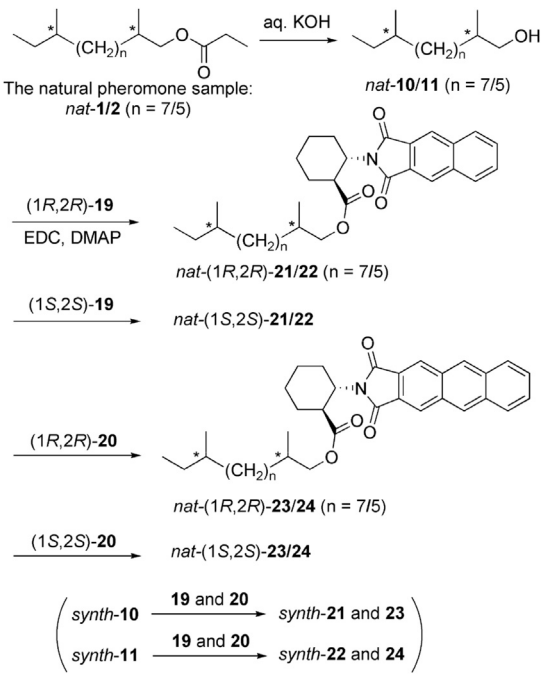
2.2. Composition of the natural pheromone of E. maslovskii

As shown in Scheme 3, the natural pheromone, which contained a mixture of **1** and **2** (*nat*-**1**/**2**), was hydrolyzed to afford the corresponding alcohols (*nat*-**10**/**11**) in order to determine its stereochemical composition via the Ohrui–Akasaka method [5]. The resulting alcohols were then esterified by treatment with Ohrui–Akasaka reagents, namely (1*R*,2*R*)- or (1*S*,2*S*)-2-(naphthalene-2,3-dicarboximido)cyclohexanecarboxylic acid (**19**, Reagent I) and (1*R*,2*R*)- or (1*S*,2*S*)-2-(anthracene-2,3-dicarboximido)cyclohexanecarboxylic acid (**20**, Reagent II), in the presence of EDC and DMAP. Reagents I (**19**) and II (**20**) are now commercially available from Tokyo Chemical Industry Co., Ltd. The prepared Ohrui–Akasaka derivatives of *nat*-**10**/**11**, i.e., *nat*-(1*R*,2*R*)-**21**/**22**, *nat*-(1*S*,2*S*)-**21**/**22**, *nat*-(1*R*,2*R*)-**23**/**24**, and *nat*-(1*S*,2*S*)-**23**/**24**, were analyzed via a 2D-HPLC system [9] (Fig. SI-1). This system is quite useful for analyzing natural products because it can remove interfering substances, reduce the run time, and improve reliability. In this system, the first column was used for the purification of the two desired fatty alcohol derivatives without disturbing their stereochemical compositions. Then, only the desired fractions were introduced into the second column to enable the separation of the stereoisomers.

The most critical issue to overcome, i.e., the scarcity of the natural sample, was achieved by thoroughly investigating the appropriate analytical conditions using *synth*-**21**–**24**. Fortunately, we found that **21**, which was prepared from 2,10-dimethyl-1-dodecanol (**10**) and Reagent I (**19**), and **24**, which was prepared from 2,8-dimethyl-1-decanol (**11**) and Reagent II (**20**), were suitable for determining the stereochemical composition of the parent compounds **10** and **11**, respectively (Fig. SI-2.).

As the results, the total composition of *nat*-**10**/**11** was determined as follows: i) the ratio of *nat*-**10** to *nat*-**11** was 70.5 to 29.5, ii) the stereochemical composition of *nat*-**10** was determined as (2*S*,10*S*):(2*S*,10*R*):(2*R*,10*S*):(2*R*,10*R*) = 0.7:91.4:1.6:6.2, and iii) the stereochemical composition of *nat*-**11** was also determined as (2*S*,8*S*):(2*S*,8*R*):(2*R*,8*S*):(2*R*,8*R*) = 69.9:1.0:11.8:17.3. Since the composition of *nat*-**10**/**11** was identical to that of the *nat*-**1**/**2**, we could clarify the total composition of the aggregation pheromone of *E. maslovskii*.



Scheme 3. Derivatization of the natural pheromone.

3. Conclusion

The synthesis of all the possible stereoisomers of 2,10-dimethyldodecyl (**1**) and 2,8-dimethyldecyl propanoate (**2**), the aggregation pheromones of *E. maslovskii*, was accomplished. This enabled us to confirm the absolute configurations of the pheromonally active compounds via bioassay analysis and to determine the total composition of the natural pheromone through careful HPLC analysis based on the Ohrui–Akasaka method. As the results, the most pheromonally active compound (2*S*,10*R*)-**1** was proven to be the most abundant (64.4%). Interestingly, the second most abundant component (20.6%) was the third most active compound (2*S*,8*S*)-**2**, and the component percentage of the second active compound, (2*S*,8*R*)-**2**, was only 0.3%.

4. Experimental section

4.1. Synthesis of *1* and *2*

4.1.1. General

All melting points were uncorrected. Melting points were recorded on a Yazawa Micro Melting Point Apparatus BY-2. Gas chromatography was performed with an Agilent 6850 GC system under the following conditions: column: Agilent HP-1, 100% dimethylpolysiloxane, 30 m length x 0.25 mm i.d., 0.25 μm df; carrier gas, N_2; flow rate, 0.7 mL min^{-1}; temp: 150–300 °C (+5 °C/min) for oxazolidinones, 70–300 °C (+5 °C/min) for other compounds. Optical rotation values were measured with a Jasco P-2300 polarimeter. NMR spectra were recorded by a JEOL JNM ECX-400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) and chemical shifts (δ) were reported using residual solvents of $CDCl_3$ as an internal standard (7.26 ppm for ^{1}H and 77.00 ppm for ^{13}C). Mass spectra were obtained with an Agilent 5977 MSD coupled with an Agilent 7890B GC system. High resolution mass spectra were measured with a JEOL JMS-T100GCV spectrometer operated in the FI mode. Kanto Kagaku silica gel 60 N (63–210 μm) was used for column chromatography. Analytical thin-layer chromatography was performed using Merck silica gel 60 F_{254} plates (0.25 mm). All air- and/or water-sensitive reactions were carried out under N_2 atmosphere in dry solvents.

4.1.2. Ethyl 10-methyldodecanoate (*6*)

To a mixture of Mg turnings (2.80 g, 115 mmol) and a piece of I_2 in THF (42.0 g), a solution of **3** (14.5 g, 96.0 mmol) in THF (43.5 g) was added dropwise at 30 °C. After stirring for 3 h, the resulting Grignard reagent was added dropwise to a solution of **4** (20.1 g, 80.0 mmol) and CuBr (0.29 g, 2.0 mmol) in NMP (31.7 g, 320 mmol) and THF (71.1 g) at 10 °C. After stirring for 3 h, the reaction mixture was poured into 20% aq. NH_4Cl solution and extracted with hexane. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was distilled to give **6** (18.7 g, 96% yield). bp 108 °C/0.08 kPa; GC t_R 23.40 min (91.5%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.83 (3H, d, J = 6.4 Hz), 0.85 (3H, t, J = 7.6 Hz), 1.05–1.15 (2H, m), 1.21–1.37 (13H, m), 1.25 (3H, t, J = 7.2 Hz), 1.61 (2H, m), 2.28 (2H, t, J = 7.6 Hz), 4.12 (2H, q, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.39, 14.24, 19.20, 24.98, 27.05, 29.14, 29.26, 29.48 (2C), 29.92, 34.38, 34.39, 36.60, 60.12, 173.92; MS (70 eV, EI) *m/z* 242 (13, M^+), 213 (17), 199 (26), 157 (40), 143 (11), 115 (10), 101 (66), 97 (16), 89 (14), 88 (100), 83 (18), 73 (14), 70 (17), 69 (15), 57 (16), 55 (17), 43 (13), 41 (12); HRMS calcd for $C_{15}H_{30}O_2$: 242.2246, found: 242.2239.

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*4.1.3. Ethyl 2,10-dimethyldodecanoate (**8**)*

To a solution of LDA, prepared from (*i*-Pr)$_2$NH (2.42 g, 24.0 mmol) and *n*-BuLi (1.57 M in hexane; 14.0 mL, 22.0 mmol) in THF (20.0 mL), a solution of **6** (4.85 g, 20.0 mmol) in THF (10.0 mL) was added dropwise at −78 °C. After stirring for 30 min, a solution of MeI (3.40 g, 24.0 mmol) and HMPA (1.08 g, 6.00 mmol) in THF (5.0 mL) was added dropwise. After stirring for 1 h, the reaction mixture was poured into 20% aq. NH_4Cl and extracted with hexane. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane/EtOAc = 20:1) to give **8** (3.69 g, 72% yield). GC t_R 23.67 min (98.2%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, d, *J* = 6.4 Hz), 0.85 (3H, t, *J* = 7.6 Hz), 1.07−1.15 (2H, m), 1.13 (3H, d, *J* = 7.2 Hz), 1.23−1.41 (14H, m), 1.25 (3H, t, *J* = 7.2 Hz), 1.66 (1H, m), 2.41 (1H, sext, *J* = 7.2 Hz), 4.13 (2H, q, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.40, 14.27, 17.07, 19.21, 27.06, 27.22, 29.49, 29.53 (2C), 29.92, 33.82, 34.38, 36.61, 39.56, 60.04, 176.99; MS (70 eV, EI) *m/z* 256 (13, M^+), 213 (10), 199 (21), 171 (19), 157 (16), 115 (55), 103 (10), 102 (100), 87 (15), 83 (10), 74 (20), 69 (13), 57 (17), 55 (14), 43 (11), 41 (11); HRMS calcd for $C_{16}H_{32}O_2$: 256.2402, found: 256.2397.

*4.1.4. 2,10-Dimethyl-1-dodecanol (**10**)*

To an ice-cooled suspension of $LiAlH_4$ (380 mg, 10.0 mmol) in Et_2O (10.0 mL), a solution of **8** (2.56 g, 10.0 mmol) in Et_2O (10.0 mL) was added dropwise at 0 °C. After stirring for 1.5 h, water (0.38 g), 15% aq. NaOH (0.38 g) and water (1.14 g) were added dropwise with vigorous stirring. After adding $MgSO_4$, the resulting mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane/EtOAc = 10:1) to give **10** (2.00 g, 93% yield). GC t_R 22.12 min (98.9%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, d, *J* = 6.4 Hz), 0.85 (3H, t, *J* = 7.6 Hz), 0.92 (3H, d, *J* = 6.8 Hz), 1.06−1.16 (3H, m), 1.21−1.42 (15H, m), 1.60 (1H, m), 3.42 (1H, dd, *J* = 10.4, 6.4 Hz), 3.51 (1H, dd, *J* = 10.4, 6.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.40, 16.58, 19.21, 26.98, 27.09, 29.49, 29.68, 29.95, 30.00, 33.15, 34.39, 35.77, 36.63, 68.44; MS (70 eV, EI) *m/z* 167 (14), 125 (22), 111 (54), 98 (13), 97 (69), 85 (37), 84 (20), 83 (62), 82 (13), 71 (77), 70 (100), 69 (70), 57 (88), 56 (39), 55 (52), 43 (39), 41 (31), 29 (10); HRMS calcd for $C_{14}H_{30}O$: 214.2297, found: 214.2280.

*4.1.5. 2,10-Dimethyldodecyl propanoate (**1**)*

To an ice-cooled solution of **10** (643 mg, 3.00 mmol) and pyridine (475 mg, 6.00 mmol) in CH_2Cl_2 (30.0 mL), propanoyl chloride (416 mg, 4.50 mmol) was added. After stirring for 1 h, the reaction mixture was poured into 5% aq. $NaHCO_3$ and extracted with hexane. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane/EtOAc = 20:1) and Kugelrohr distillation to give (±)-**1** (775 mg, 96% yield). GC t_R 26.52 min (99.0%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, d, *J* = 6.4 Hz), 0.85 (3H, t, *J* = 7.2 Hz), 0.92 (3H, d, *J* = 6.8 Hz), 1.06−1.18 (3H, m), 1.15 (3H, t, *J* = 7.6 Hz), 1.21−1.40 (14H, m), 1.77 (1H, m), 2.33 (2H, q, *J* = 7.6 Hz), 3.86 (1H, dd, *J* = 10.8, 6.8 Hz), 3.95 (1H, dd, *J* = 10.8, 6.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.20, 11.39, 16.87, 19.21, 26.81, 27.08, 27.65, 29.49, 29.63, 29.83, 29.97, 32.55, 33.36, 34.39, 36.62, 69.30, 174.63; MS (70 eV, EI) *m/z* 167 (22), 125 (15), 111 (45), 97 (50), 86 (10), 85 (18), 84 (14), 83 (41), 75 (33), 71 (38), 70 (66), 69 (39), 57 (100), 56 (34), 55 (27), 43 (16), 41 (15), 29 (11); HRMS calcd for $C_{17}H_{34}O_2$: 270.2559, found: 270.2539.

*4.1.6. Ethyl 8-methyldecanoate (**7**)*

In the same manner as described for the synthesis of **6**, **3** (14.5 g, 96.0 mmol) was converted to **7** (16.7 g, 97% yield). bp 62−71 °C/0.1 kPa; GC t_R 18.46 min (98.0%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, d, *J* = 6.4 Hz), 0.85 (3H, t, *J* = 7.6 Hz), 1.06−1.15 (2H, m), 1.21−1.36 (9H, m), 1.25 (3H, t, *J* = 7.6 Hz), 1.62 (2H, quint, *J* = 7.6 Hz), 2.29 (2H, t, *J* = 7.6 Hz), 4.12 (2H, q, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.38, 14.25, 19.19, 25.00, 26.89, 29.18, 29.47, 29.60, 34.36, 34.40, 36.53, 60.13, 173.92; MS (70 eV, EI) *m/z* 187 (11), 186 (15), 169 (20), 151 (16), 139 (11), 129 (29), 95 (25), 83 (11), 71 (54), 70 (100), 69 (13), 57 (18), 55 (21), 43 (31), 41 (15); HRMS calcd for $C_{13}H_{26}O_2$: 214.1933, found: 214.1934.

*4.1.7. Ethyl 2,8-dimethyldecanoate (**9**)*

In the same manner as described for the synthesis of **8**, **7** (4.85 g, 20.0 mmol) was converted to **9** (1.00 g, 47% yield). GC t_R 19.18 min (96.3%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, t, *J* = 6.4 Hz), 0.85 (3H, t, *J* = 7.6 Hz), 1.06−1.15 (2H, m), 1.14 (3H, d, *J* = 6.8 Hz), 1.23−1.43 (10H, m), 1.25 (3H, t, *J* = 7.2 Hz), 1.64 (1H, m), 2.41 (1H, sext, *J* = 6.8 Hz), 4.13 (2H, q, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.37, 14.25, 17.05, 19.17, 26.91, 27.25, 29.46, 29.85, 33.82, 34.35, 36.52, 39.55, 60.02, 176.94; MS (70 eV, EI) *m/z* 228 (5, M^+), 183 (11), 171 (49), 157 (13), 129 (15), 115 (68), 103 (11), 102 (100), 97 (10), 87 (23), 83 (14), 74 (31), 71 (11), 69 (19), 57 (24), 55 (20), 43 (14), 41 (18), 29 (11); HRMS calcd for $C_{14}H_{28}O_2$: 228.2089, found: 228.2108.

*4.1.8. 2,8-Dimethyl-1-decanol (**11**)*

In the same manner as described for the synthesis of **10**, **9** (0.80 g, 3.5 mmol) was converted to **11** (0.62 g, 95% yield). GC t_R 17.39 min (99.0%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, d, *J* = 6.0 Hz), 0.86 (3H, t, *J* = 7.6 Hz), 0.92 (3H, t, *J* = 6.4 Hz), 1.07−1.17 (3H, m), 1.21−1.42 (10H, m), 1.48 (1H, br), 1.61 (1H, m), 3.42 (1H, dd, *J* = 10.8, 6.8 Hz), 3.50 (1H, dd, *J* = 10.8, 6.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.37, 16.56, 19.19, 27.01, 27.05, 29.46, 29.47, 30.27, 30.28, 33.15, 34.37, 35.75, 36.59, 68.38; MS (70 eV, EI) *m/z* 139 (22), 111 (12), 98 (15), 97 (48), 85 (24), 84 (20), 83 (82), 71 (62), 70 (100), 69 (58), 57 (91), 56 (37), 55 (54), 43 (40), 41 (32), 29 (11); HRMS calcd for $C_{12}H_{26}O$: 186.1984, found: 186.1977.

*4.1.9. 2,8-Dimethyldecyl propanoate (**2**)*

In the same manner as described for the synthesis of **1**, **11** (250 mg, 1.34 mmol) was converted to **2** (0.31 g, 95% yield). GC t_R 22.17 min (98.8%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, d, *J* = 6.4 Hz), 0.86 (3H, t, *J* = 7.6 Hz), 0.92 (3H, d, *J* = 6.8 Hz), 1.07−1.14 (3H, m), 1.15 (3H, t, *J* = 7.6 Hz), 1.21−1.38 (10H, m), 1.77 (1H, m), 2.33 (2H, q, *J* = 7.6 Hz), 3.86 (1H, dd, *J* = 10.8, 6.8 Hz), 3.95 (1H, dd, *J* = 10.8, 6.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.18, 11.38, 16.86, 19.19, 26.83, 27.00, 27.63, 29.46, 30.15, 30.16, 32.54, 33.36, 34.37, 36.56, 69.28, 174.61; MS (70 eV, EI) *m/z* 140 (11), 139 (36), 111 (13), 98 (11), 97 (33), 85 (10), 84 (15), 83 (56), 75 (27), 71 (30), 70 (64), 69 (32), 57 (100), 56 (31), 55 (25), 43 (14), 41 (14), 29 (12); HRMS calcd for $C_{15}H_{30}O_2$: 242.2246, found: 242.2231.

*4.1.10. Ethyl (S)-10-methyldodecanoate [(S)-**6**]*

In the same manner as described for the synthesis of **6**, (*S*)-**3** (18.0 g, 119 mmol) was converted to (*S*)-**6** (25.4 g). GC t_R 23.30 min (96.8%); $[\alpha]_D^{20}$ +5.65 (*c* = 1.75 in $CHCl_3$); HRMS calcd for $C_{15}H_{30}O_2$: 242.2246, found: 242.2254.

*4.1.11. (S)-10-Methyldodecanoic acid [(S)-**12**]*

To a solution of (*S*)-**6** (25.2 g) in THF (120 mL) was added 20% aq. NaOH (120 g, 0.60 mol). The mixture was heated under reflux for 5 h. After the reaction mixture was cooled to room temperature, the aqueous layer was separated and washed with Et_2O. The aqueous layer was acidified with 1 M aq. HCl and extracted with Et_2O. The extract was washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure to give (*S*)-**12** (20.8 g). GC t_R 23.48 min (99.2%); $[\alpha]_D^{20}$ +6.13 (*c* = 1.86 in $CHCl_3$); ^{1}H NMR ($CDCl_3$,

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400 MHz) δ 0.84 (3H, d, $J = 6.4$ Hz), 0.85 (3H, t, $J = 7.6$ Hz), 1.05–1.15 (2H, m), 1.20–1.38 (13H, m), 1.63 (2H, quint, $J = 7.6$ Hz), 2.35 (2H, t, $J = 7.6$ Hz), 10.67 (1H, br); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.40, 19.21, 24.67, 27.05, 29.05, 29.24, 29.46, 29.49, 29.92, 33.97, 34.38, 36.60, 179.70; MS (70 eV, EI) *m/z* 214 (20, M^+), 185 (63), 171 (39), 167 (59), 159 (13), 158 (13), 157 (22), 149 (73), 140 (24), 129 (98), 125 (37), 116 (26), 115 (44), 111 (31), 109 (12), 107 (11), 101 (32), 99 (21), 98 (23), 97 (66), 96 (57), 95 (14), 93 (10), 87 (25), 85 (37), 84 (17), 83 (82), 81 (16), 73 (81), 71 (47), 70 (24), 69 (71), 67 (11), 60 (52), 57 (100), 56 (34), 55 (71), 43 (57), 42 (10), 41 (56), 29 (20); HRMS calcd for $C_{13}H_{26}O_2$: 214.1933, found: 214.1938.

4.1.12. (4*S*,10′*S*)–*N*-[10′-Methyldodecanoyl]-4-benzyl-2-oxazolidinone [(4*S*,10′*S*)-**15**]

A solution of (*S*)-**12** (6.90 g) in $(COCl)_2$ (4.08 g, 32.2 mmol) was stirred for 16 h at room temperature. The reaction mixture was concentrated under reduced pressure to give the corresponding acyl chloride (7.68 g). To a cooled solution of (*S*)-**14** (6.28 g, 35.4 mmol) in THF (100 mL), *n*-BuLi (1.57 M in hexane; 23.6 mL, 37.2 mmol) was added dropwise at −78 °C. After stirring for 30 min, a solution of the above-prepared acyl chloride in THF (20.0 mL) was added dropwise. After removal of cooling-bath, the stirring was continued for 16 h. The reaction mixture was then poured into 20% aq. NH_4Cl and extracted with Et_2O. The organic layer was washed with 5% aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane/EtOAc = 5:1) to give (4*S*,10′*S*)-**15** (7.80 g, 63% yield in 4 steps from (*S*)-**3**). GC t_R 27.20 min (95.8%); m.p. 44 °C; $[\alpha]_D^{20}$ +41.0 ($c = 3.12$ in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, d, $J = 6.4$ Hz), 0.85 (3H, t, $J = 7.2$ Hz), 1.05–1.17 (2H, m), 1.21–1.41 (13H, m), 1.60–1.73 (2H, m), 2.76 (1H, dd, $J = 13.2$, 9.6 Hz), 2.85–3.01 (2H, m), 3.30 (1H, dd, $J = 13.2$, 3.2 Hz), 4.15–4.22 (2H, m), 4.67 (1H, m), 7.21 (2H, m), 7.25–7.36 (3H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.40, 19.21, 24.27, 27.07, 29.13, 29.40, 29.48, 29.52, 29.95, 34.38, 35.53, 36.61, 37.93, 55.15, 66.13, 127.32, 128.94 (2C), 129.41 (2C), 135.33, 153.45, 173.46; MS (70 eV, EI) *m/z* 373 (8, M^+), 282 (19), 219 (23), 198 (15), 197 (100), 179 (13), 178 (24), 134 (12), 123 (18), 117 (18), 109 (19), 97 (22), 95 (12), 91 (11), 83 (15), 71 (11), 57 (18), 55 (10); HRMS calcd for $C_{23}H_{35}NO_3$: 373.2617, found: 373.2626.

4.1.13. (4*S*,2′*S*,10′*S*)–*N*-[(2′,10′-Dimethyldodecanoyl]-4-benzyl-2-oxazolidinone [(4*S*,2′*S*,10′*S*)-**17**]

To a cooled solution of (4*S*,10′*S*)-**15** (4.32 g, 11.6 mmol) in THF (120 mL), NaHMDS (1.0 M in THF; 12.8 mL, 12.8 mmol) was added dropwise at −78 °C. Subsequently, MeI (8.20 g, 57.8 mmol) was added to the mixture. After removal of cooling-bath, the reaction mixture was stirred for 16 h, poured into 20% aq. NH_4Cl, and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The Rf values of the major (2′*S*)- and minor (2′*R*)-isomers were 0.38 and 0.27 (eluent: *n*-hexane/AcOEt = 5:1), respectively. The residue was purified by silica-gel column chromatography (hexane/EtOAc = 10:1) to give (4*S*,2′*S*,10′*S*)-**17** (3.11 g, 69% yield). GC t_R 27.09 min (99.2%); $[\alpha]_D^{20}$ +63.3 ($c = 1.65$ in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.83 (3H, d, $J = 6.4$ Hz), 0.85 (3H, t, $J = 7.6$ Hz), 1.05–1.15 (2H, m), 1.21–1.45 (14H, m), 1.22 (3H, d, $J = 6.8$ Hz), 1.73 (1H, m), 2.77 (1H, dd, $J = 13.2$, 9.6 Hz), 3.27 (1H, dd, $J = 13.2$, 3.2 Hz), 3.70 (1H, sext, $J = 6.8$ Hz), 4.15–4.22 (2H, m), 4.68 (1H, m), 7.22 (2H, m), 7.25–7.36 (3H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.40, 17.36, 19.21, 27.07, 27.27, 29.48, 29.55, 29.67, 29.93, 33.44, 34.38, 36.60, 37.71, 37.91, 55.36, 65.99, 127.32, 128.92 (2C), 129.44 (2C), 135.35, 153.06, 177.37; MS (70 eV, EI) *m/z* 387 (6, M^+), 296 (10), 233 (32), 212 (16), 211 (100), 183 (22), 178 (27), 117 (13), 113 (12), 99 (13), 85 (20), 71 (23), 57 (24); HRMS calcd for $C_{24}H_{37}NO_3$: 387.2773, found: 387.2781.

4.1.14. (2*S*,10*S*)-2,10-Dimethyl-1-dodecanol [(2*S*,10*S*)-**10**]

To an ice-cooled suspension of $LiAlH_4$ (490 mg, 12.9 mmol) in THF (25.0 mL), a solution of (4*S*,2′*S*,10′*S*)-**17** (2.00 g, 5.16 mmol) in THF (10.0 mL) was added dropwise. After stirring for 16 h, the reaction mixture was quenched by addition of water (0.49 g) and then dissolved by addition of 2 M aq. HCl. The resulting mixture was extracted with Et_2O. The organic layer was washed with 5% aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane/EtOAc = 10:1) to give (2*S*,10*S*)-**10** (1.00 g, 91% yield). GC t_R 21.99 min (99.4%); $[\alpha]_D^{20}$ −1.76 ($c = 1.81$ in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, d, $J = 6.4$ Hz), 0.85 (3H, t, $J = 7.2$ Hz), 0.92 (3H, d, $J = 6.8$ Hz), 1.06–1.16 (3H, m), 1.21–1.43 (15H, m), 1.60 (1H, m), 3.41 (1H, dd, $J = 10.4$, 6.4 Hz), 3.51 (1H, dd, $J = 10.4$, 5.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.39, 16.57, 19.20, 26.98, 27.09, 29.48, 29.68, 29.95, 30.00, 33.14, 34.38, 35.75, 36.62, 68.41; HRMS calcd for $C_{14}H_{30}O$: 214.2297, found: 214.2282.

4.1.15. (2*S*,10*S*)-2,10-Dimethyldodecyl propanoate [(2*S*,10*S*)-**1**]

In the same manner as described for the synthesis of **1**, (2*S*,10*S*)-**10** (800 mg, 3.73 mmol) was converted to (2*S*,10*S*)-**1** (841 mg, 83% yield). GC t_R 26.52 min (99.3%); $[\alpha]_D^{20}$ +5.23 ($c = 1.73$ in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, d, $J = 6.4$ Hz), 0.85 (3H, t, $J = 7.6$ Hz), 0.92 (3H, d, $J = 6.8$ Hz), 1.06–1.18 (3H, m), 1.15 (3H, t, $J = 7.6$ Hz), 1.21–1.39 (14H, m), 1.77 (1H, m), 2.33 (2H, q, $J = 7.6$ Hz), 3.85 (1H, dd, $J = 10.8$, 7.2 Hz), 3.96 (1H, dd, $J = 10.8$, 6.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.19, 11.38, 16.86, 19.20, 26.81, 27.08, 27.64, 29.48, 29.62, 29.83, 29.97, 32.54, 33.36, 34.38, 36.61, 69.29, 174.62. HRMS calcd for $C_{17}H_{34}O_2$: 270.2559, found: 270.2547.

Subsequently, in the same manner, (2*R*,10*S*)-, (2*S*,10*R*)-, and (2*R*,10*R*)-**1** were synthesized. (See SI).

4.1.16. Ethyl (*S*)-8-methyldecanoate [(*S*)-**7**]

In the same manner as described for the synthesis of **6**, (*S*)-**3** (15.0 g, 99.0 mmol) was converted to (*S*)-**7** (21.8 g). GC t_R 18.72 min (96.0%); [α]20D +6.82 ($c = 1.81$ in $CHCl_3$); HRMS calcd for $C_{13}H_{26}O_2$: 214.1933, found: 214.1949.

4.1.17. (*S*)-8-Methyldecanoic acid [(*S*)-**13**]

In the same manner as described for the synthesis of (*S*)-**12**, (*S*)-**7** (21.8 g) was converted to (*S*)-**13** (14.2 g). GC t_R 19.21 min (99.4%); $[\alpha]_D^{20}$ +7.44 ($c = 1.78$ in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, d, $J = 6.4$ Hz), 0.85 (3H, t, $J = 7.2$ Hz), 1.08–1.18 (2H, m), 1.21–1.38 (9H, m), 1.64 (2H, quint, $J = 7.6$ Hz), 2.35 (2H, t, $J = 7.6$ Hz), 10.69 (1H, br); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.39, 19.19, 24.68, 26.86, 29.09, 29.47, 29.57, 33.92, 34.36, 36.52, 179.39; MS (70 eV, EI) *m/z* 186 (4, M^+), 157 (10), 139 (47), 130 (15), 129 (100), 121 (22), 111 (12), 101 (21), 98 (14), 97 (43), 95 (10), 87 (31), 85 (17), 83 (19), 81 (11), 73 (57), 71 (27), 69 (42), 60 (25), 57 (39), 56 (15), 55 (38), 43 (25), 41 (28), 29 (11); HRMS calcd for $C_{11}H_{22}O_2$: 186.1620, found: 186.1630.

4.1.18. (4*S*,8′*S*)–*N*-[(8′-Methyldecanoyl]-4-benzyl-2-oxazolidinone [(4*S*,8′*S*)-**16**]

In the same manner as described for the synthesis of (4*S*,10′*S*)-**15**, (*S*)-**13** (6.00 g) was converted to (4*S*,8′*S*)-**16** (8.00 g, 67% yield in 4 steps from (*S*)-**3**). GC t_R 24.17 min (94.4%); m.p. 56 °C; $[\alpha]_D^{20}$ +45.2 ($c = 1.63$ in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, d, $J = 6.0$ Hz), 0.86 (3H, t, $J = 7.2$ Hz), 1.06–1.17 (2H, m), 1.22–1.43 (9H, m), 1.60–1.74 (2H, m), 2.77 (1H, dd, $J = 13.2$, 9.6 Hz), 2.85–3.01 (2H, m), 3.30 (1H, dd, $J = 13.2$, 3.2 Hz), 4.14–4.22 (2H, m), 4.68 (1H, m),

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7.21 (2H, m), 7.25–7.36 (3H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.39, 19.20, 24.28, 26.92, 29.17, 29.47, 29.73, 34.37, 35.54, 36.54, 37.94, 55.15, 66.13, 127.33, 128.94 (2C), 129.41 (2C), 135.33, 153.45, 173.45; MS (70 eV, EI) *m/z* 345 (9, M^+), 254 (29), 219 (26), 178 (23), 170 (13), 169 (100), 151 (44), 134 (15), 117 (22), 116 (11), 109 (14), 95 (52), 91 (15), 83 (14), 81 (17), 69 (12), 57 (17), 55 (13), 43 (12); HRMS calcd for $C_{21}H_{31}NO_3$: 345.2304, found: 345.2297.

4.1.19. (4*S*,2′*S*,8′*S*)–*N*-[(2′,8′-Dimethyldecanoyl]-4-benzyl-2-oxazolidinone [(4*S*,2′*S*,8′*S*)-**18**]

In the same manner as described for the synthesis of (4*S*,2′*S*,10′*S*)-**17**, (4*S*,8′*S*)-**16** (4.00 g, 11.6 mmol) was converted to (4*S*,2′*S*,8′*S*)-**18** (3.14 g, 78% yield). The ratio of (2′*S*)- and (2′*R*)-isomers in crude **18** was 96:4. The Rf values of each isomers were 0.47 and 0.33 (eluent: hexane/EtOAc = 5:1), respectively. GC t_R 24.04 min (99.5%); $[\alpha]_D^{20}$ +65.3 (c = 1.84 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.83 (3H, d, J = 6.4 Hz), 0.85 (3H, t, J = 7.2 Hz), 1.04–1.15 (2H, m), 1.22–1.44 (10H, m), 1.22 (3H, d, J = 6.8 Hz), 1.73 (1H, m), 2.77 (1H, dd, J = 13.2, 9.6 Hz), 3.27 (1H, dd, J = 13.2, 3.2 Hz), 3.71 (1H, sext, J = 6.8 Hz), 4.14–4.22 (2H, m), 4.68 (1H, m), 7.21 (2H, m), 7.25–7.36 (3H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.39, 17.35, 19.19, 26.94, 27.31, 29.46, 30.00, 33.45, 34.36, 36.53, 37.71, 37.92, 55.36, 65.99, 127.32, 128.92 (2C), 129.44 (2C), 135.35, 153.06, 177.37; MS (70 eV, EI) *m/z* 359 (7, M^+), 268 (17), 233 (34), 184 (14), 183 (100), 178 (26), 155 (20), 117 (15), 99 (16), 91 (11), 85 (26), 71 (23), 57 (27), 55 (10); HRMS calcd for $C_{22}H_{33}NO_3$: 359.2460, found: 359.2466.

4.1.20. (2*S*,8*S*)-2,8-Dimethyl-1-decanol [(2*S*,8*S*)-**11**]

In the same manner as described for the synthesis of (2*S*,10*S*)-**10**, (4*S*,2′*S*,8′*S*)-**18** (800 mg, 2.23 mmol) was converted to (2*S*,8*S*)-**11** (410 mg, 99% yield). GC t_R 17.26 min (98.8%); $[\alpha]_D^{20}$ −2.16 (c = 1.71 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, d, J = 6.4 Hz), 0.85 (3H, t, J = 7.2 Hz), 0.92 (3H, d, J = 6.8 Hz), 1.05–1.16 (3H, m), 1.21–1.42 (10H, m), 1.57 (1H, s), 1.60 (1H, m), 3.42 (1H, m), 3.51 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.40, 16.59, 19.22, 27.02, 27.07, 29.48, 30.29, 33.16, 34.39, 35.78, 36.61, 68.44; HRMS calcd for $C_{12}H_{26}O$: 186.1984, found: 186.1969.

4.1.21. (2*S*,8*S*)-2,8-Dimethyldecyl propanoate [(2*S*,8*S*)-**2**]

In the same manner as described for the synthesis of **1**, (2*S*,8*S*)-**11** (300 mg, 1.61 mmol) was converted to (2*S*,8*S*)-**2** (368 mg, 94% yield). GC t_R 22.25 min (98.9%); $[\alpha]_D^{20}$ +6.06 (c = 1.47 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (3H, d, J = 6.4 Hz), 0.86 (3H, t, J = 7.6 Hz), 0.92 (3H, d, J = 6.4 Hz), 1.06–1.18 (3H, m), 1.15 (3H, t, J = 7.6 Hz), 1.21–1.39 (10H, m), 1.77 (1H, m), 2.33 (2H, q, J = 7.6 Hz), 3.85 (1H, dd, J = 10.4, 6.8 Hz), 3.96 (1H, dd, J = 10.4, 6.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.20, 11.39, 16.88, 19.21, 26.84, 27.01, 27.65, 29.47, 30.17, 32.55, 33.37, 34.38, 36.57, 69.30, 174.64; HRMS calcd for $C_{15}H_{30}O_2$: 242.2246, found 242.2254.

Subsequently, in the same manner, (2*R*,8*S*)-, (2*S*,8*R*)-, and (2*R*,8*R*)-**2** were also synthesized. (See SI).

4.2. Composition of the natural pheromone of *E. maslovskii*

4.2.1. Saponification and derivatization of the naturally occurring pheromone

The natural pheromone sample collected from 2500 females (probably containing 10–15 ng of *nat*-**1**/**2**; see Ref. [4]) was dissolved in isooctane/2-propanol (1:1; 0.8 mL). A 0.2 mL aliquot was added to the test tube, followed by 0.1 M KOH (in EtOH; 2.0 mL) and distilled water (0.2 mL). The test tube was stood at 90 °C for 40 min without capping. After saponification, the residual solvent was removed under CO_2 gas stream. The residue was dissolved in hexane/diisopropyl ether (IPE) (3:1; 2.0 mL) and washed with sat. $NaHCO_3$ solution (3.0 mL). The desired alcohols were extracted from the aqueous layer twice with hexane/IPE (3:1; 2.0 mL). The combined organic layer was washed with sat. $NaHCO_3$ solution (2.0 mL), and the separated aqueous layer was extracted with hexane/IPE (3:1; 2.0 mL). The combined organic layer was washed with brine (2.0 mL), and the separated aqueous layer was extracted with hexane/IPE (3:1; 2.0 mL). Finally, the combined organic layer was concentrated under reduced pressure. The resultant residue (containing *nat*-**10**/**11**) was dissolved in toluene/CH_3CN (1:1; 1.0 mL), and a 0.5 mL aliquot was esterified by treatment with (1*R*,2*R*)-**19** (large excess amount), in the presence of EDC (large excess amount) and DMAP (cat. amount) at 35 °C for more than 6 h. After completion of reaction, the reaction mixture was loaded onto a silica gel TLC plate (0.2 mm, 10 × 20 cm, Merck art 5554) and developed with hexane/EtOAc (5:1, v/v). The desired fraction was collected, packed into the short column, and eluted with EtOH/EtOAc (1:1, v/v). The eluate was concentrated to ca. 0.1 mL under Ar stream, and diluted with MeOH (0.05 mL) to furnish the sample solution of *nat*-(1*R*,2*R*)-**21**/**22**. In the same manner, the solution of *nat*-(1*S*,2*S*)-**21**/**22** was prepared by using (1*S*,2*S*)-**19**. The solutions of *nat*-(1*R*,2*R*)-**23**/**24** and *nat*-(1*S*,2*S*)-**23**/**24** were also prepared by condensation with **20** instead of **19**.

4.2.2. Stereoisomer separations by 2D-HPLC system

Fig. SI-1 shows the 2D-HPLC system employed for these analyses. By using this system, stereoisomer separations of the above-prepared derivatives (**21**–**24**) were performed under low column temperature conditions. Based on our preliminary investigations on stereoisomer separation employing *synth*-**21**–**24**, **21** and **24** were suitable for determination of their stereochemical compositions of **10** and **11**, respectively. (Fig. SI-2).

The derivatives **21** were used to determine the stereochemical composition of *nat*-**10**. A solution of *nat*-**21**/**22** (10 μL) was separated on a Develosil ODS-HG-3 column (Nomura chemicals, 4.6 mm i.d. x 150 mm) eluted with MeOH/CH_3CN (3:7, v/v) at 0.12 mL min^{-1} and 0 °C (in an ice bath). The desired fractions between 63.0 and 68.0 min, and between 100.0 and 110.0 min were loaded onto the second columns via a column switching device (PT-8000, Tosoh), and then separated on the Develosil ODS-HG-3 columns (3.0 mm i.d. x 250 mm and 3.0 mm i.d. x 150 mm in series) eluted with MeOH/CH_3CN/THF (48:28:24, v/v/v) at 0.12 mL min^{-1} and −45 °C (cooled by Cryocool CC-100 equipped with Cryotrol). Detection was performed by a fluorescence detector FP-4025 (JASCO, excitation at 262 nm and emission at 380 nm). Pumps used were PU-920 (JASCO) and L2130 (Hitachi), and the autosampler was L-2200 (Hitachi).

The derivatives **24** were used to determine the stereochemical composition of *nat*-**11**. A solution of *nat*-**23**/**24** (10 μL) was separated on a Develosil ODS-HG-3 column (4.6 mm i.d. x 150 mm) eluted with MeOH/CH_3CN (3:7, v/v) at 0.12 mL min^{-1} and 0 °C. The desired fraction between 104.5 min and 115.0 min was loaded onto the second columns via a column switching device, and then separated on the Develosil ODS-HG-3 columns (3.0 mm i.d. x 250 mm and 3.0 mm i.d. x 150 mm in series) eluted with MeOH/THF (73:27, v/v) at 0.10 mL min^{-1} and −40 °C. Detection was performed by fluorescence detector (excitation at 298 nm and emission at 460 nm).

Although *synth*-**22** gave a single peak at 167 min, *synth*-**21** were separated into four peaks (Fig. SI-3).

The ratio of *nat*-**10**:*nat*-**11** was estimated to be 70.5:29.5, which was average of data (n = 4) obtained by using *nat*-(1*R*,2*R*)- **21**/**22** and *nat*-(1*S*,2*S*)-**21**/**22** (Fig. SI-4).

In the separation of *nat*-(1*R*,2*R*)-**21**, 2nd peak overlapped 3rd peak because 2nd peak was much larger than 3rd peak, resulting a single peak. Therefore, the peak area of 2nd peak was the sum of

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that of (2*S*,10*R*)- and (2*R*,10*R*)-**21**. On the other hand, *nat*-(1*S*,2*S*)-**21** gave four peaks and separated into each stereoisomer. Thus, the stereochemical composition of *nat*-**10** could be determined as (2*S*,10*R*):(2*R*,10*R*):(2*R*,10*S*):(2*S*,10*S*) = 91.4:6.2:1.6:0.7 (Fig. SI-5).

Synth-**24** could be separated into three peaks instead of four (Fig. SI-6). However, it was possible to determine the ratio of four stereoisomers from the results obtained with both *nat*-(1*R*,2*R*)-**24** and *nat*-(1*S*,2*S*)-**24**. (Fig. SI-7) The stereochemical composition of *nat*-**11** was (2*S*,8*S*):(2*R*,8*R*):(2*R*,8*S*):(2*S*,8*R*) = 69.9:17.3:11.8:1.0.

The complete composition of the pheromone of *E. maslovskii* was summarized in Table in Fig. SI-8.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2020.131410.

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