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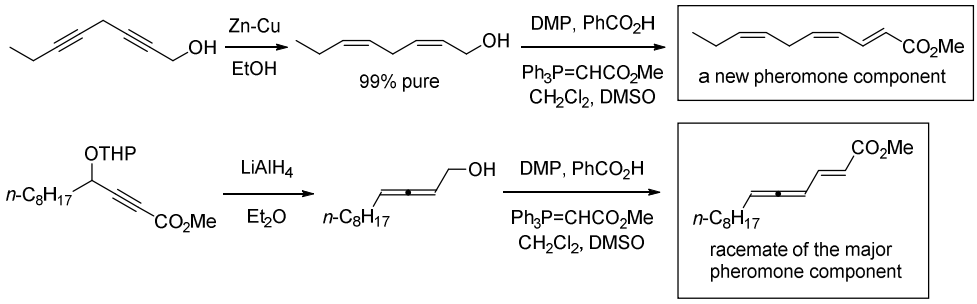

K. Mori, Graphical Abstract.

Pheromone synthesis. Part 257: Synthesis of methyl (2*E*,4*Z*,7*Z*)-2,4,7-decatrienoate and methyl (*E*)-2,4,5-tetradecatrienoate, the pheromone components of the male dried bean beetle, *Acanthoscelides obtectus* (Say)☆

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ABSTRACT

Tandem Dess-Martin oxidation/Wittig reaction of (2*Z*,5*Z*)-2,5-octadien-1-ol yielded methyl (2*E*,4*Z*,7*Z*)-2,4,7-decatrienoate, a newly discovered pheromone component of the male dried bean beetle, while that of (±)-2,3-dodecadien-1-ol gave (±)-methyl (*E*)-2,4,5-tetradecatrienoate, the racemate of the known and major pheromone component. Methyl (2*E*,4*E*,7*Z*)-2,4,7-decatrienoate was also synthesized, which is the methyl ester of an acid metabolite of a green alga. Reduction of 2,5-octadiyn-1-ol with Zn-Cu/EtOH cleanly gave (2*Z*,5*Z*)-2,5-octadien-1-ol.

☆ For Part 256, see Ref. 1.

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1. Introduction

In 1970 Horler isolated (−)-methyl (*E*)-2,4,5-tetradecatrienoate (**1**, Fig.1) as the male pheromone of the dried bean beetle, *Acanthoscelides obtectus* (Say)[Coleoptera: Bruchidae].[2] This chiral and non-racemic allene attracted the attention of chemists, and a number of synthesis of (±)-, (*R*)- and (*S*)-**1** were reported to date as detailed in ref. 3 and references cited therein.

The absolute configuration of **1** was definitely determined as *R* (87% ee) by my synthesis of the enantiomers of **1**[3] followed by their GC comparison with the naturally occurring **1**.[4] Although (*R*)-**1** was electroantennographically bioactive, it did not attract females, indicating that there must be additional pheromone components. International cooperative investigations carried out by several research groups culminated in the identification of two additional methyl esters **2** and **3** along with three other active compounds.[4] A mixture of all six components in natural proportions proved to be behaviorally bioactive as the pheromone of the dried bean beetle.[4] As reported previously,[3] the synthesis of **2** could be accomplished smoothly. However, the synthesis of **3**, a new compound, was not at all easy despite its seemingly simple structure, because of its high tendency to isomerize.

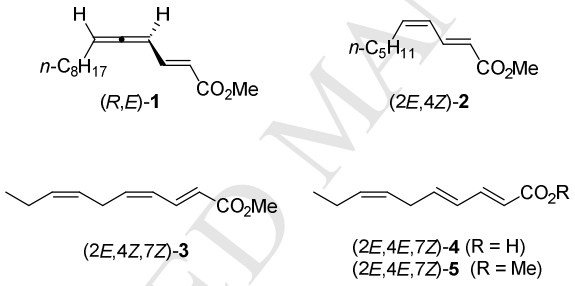


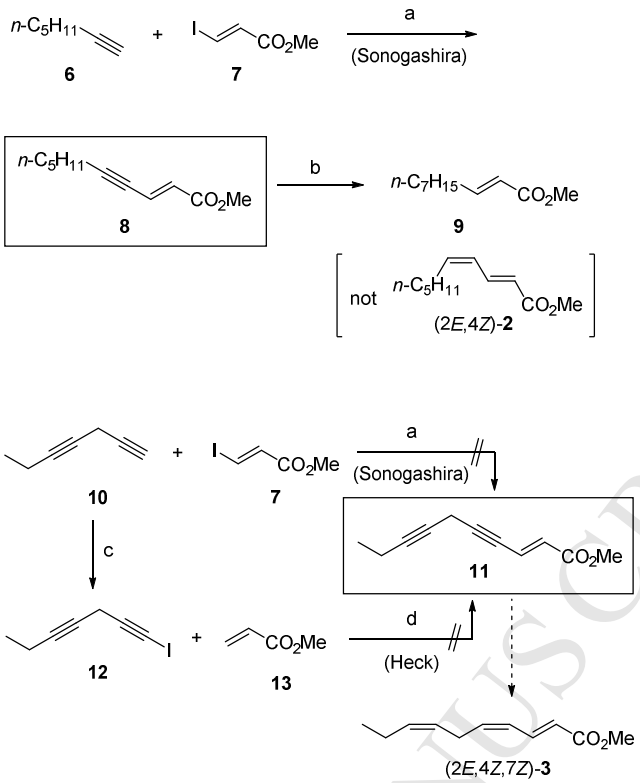
Fig. 1. Structures **1**, **2** and **3** of the pheromone components of the male dried bean beetle, *Acanthoscelides obtectus*, and structure **4** of a metabolite of the green alga, *Cladophora columbiana*.

The first objective of this paper is to report the synthesis of methyl (2*E*,4*Z*,7*Z*)-2,4,7-decatrienoate (**3**) and its (2*E*,4*E*,7*Z*)-isomer (**5**). The latter is the esterification product of an acid metabolite **4** of the green alga, *Cladophora columbiana*.[5] The second objective is to describe a concise synthesis of (±)-**1** by modification of Landor's 1971 route.[6] An attempted preparation of (*S*)-**1** is also recorded.

2. Results and discussion

2.1. Attempted synthesis of 2 and 3 via organopalladium chemistry

As shown in Scheme 1, the pheromone components **2** and **3** seemed to be obtainable from intermediates **8** and **11**, which were to be prepared by either Sonogashira coupling[7] or Heck reaction.[8]



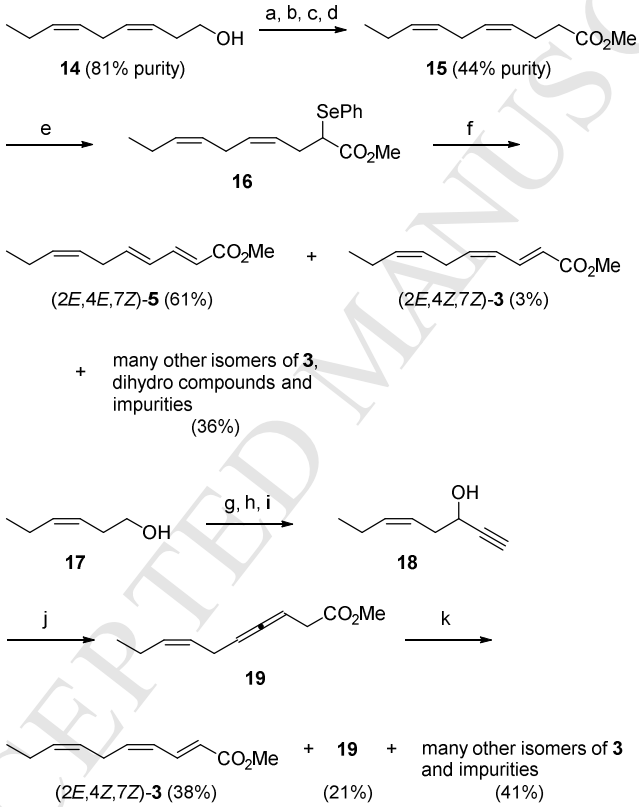
Scheme 1. Attempts to prepare **2** and **3** via organopalladium chemistry. Reagents: (a) $PdCl_2(Ph_3P)_2$, CuI, Et_3N, THF (50% for **8**); (b) H_2, $Pd/BaSO_4$, quinolone, MeOH (45%); (c) I_2, morpholine, C_6H_6 (27%); (d) $Pd(OAc)_2$, K_2CO_3, $(n\text{-}Bu)_4NCl$, DMF.

Firstly, an attempt was made to execute the Sonogashira coupling between 1-heptyne (**6**) and methyl β-iodoacrylate (**7**)[9], which was successful to give the desired ester **8** in 50% yield. Semi-hydrogenation of **8** was expected to give the pheromone component **2**. Unfortunately, however, hydrogenatgion of **8** over $Pd/BaSO_4$ in the presence of quinoline in MeOH[10] yielded the over-reduction product **9** instead of the desired **2**.

Secondly, the Sonogashira coupling of 1,4-heptadiyne (**10**)[11] with methyl β-iodoacrylate (**7**) was attempted employing $PdCl_2(Ph_3P)_2$ and CuI as catalysts in the presence of Et_3N in THF. Unfortunately, the reaction gave only a dark and obscure mixture of products, and **11** could not be secured. The next attempt was the Heck reaction of 1-iodo-1,4-heptadiyne (**12**) with methyl acrylate (**13**). In this attempt, too, no useful product such as **11** could be obtained. It therefore seemed that the presence of the skipped diyne system in **10** and **12** was the major reason for the failure to obtain **11**. Thus, organopalladium chemistry turned out to be of no use in this particular case.

2.2. Attempted application of the two successful routes for the synthesis of 1 and 2 to the synthesis of 3

In my previous synthesis of **1**, organoselenium chemistry was successfully employed to introduce the (*E*)-double bond at C-2 of **1**.[3] It was therefore expected that ester **15** (Scheme 2) would give (2*E*,4*Z*,7*Z*)-**3** via α-phenylselenenyl ester **16**. The starting (3*Z*,6*Z*)-3,6-nonadien-1-ol (**14**) was prepared by the known method.[12] Its purity, however, was only 81% with 18% of the isomers of nonen-1-ol, the over-reduction products generated in the course of the semi-hydrogenation of 3,6-nonadiyn-1-ol. The impure dienol **14** was then converted to methyl (4*Z*,7*Z*)-4,7-decadienoate (**15**) after four synthetic operations: (i) tosylation, (ii) treatment with KCN, (iii) alkaline hydrolysis with NaOH in refluxing aq. EtOH, and (iv) esterification with CH_2N_2. The resulting **15** was only 44% pure, contaminated with (4*E*,7*Z*)-isomer (20%) and others. Presumably, heating under alkaline conditions to hydrolyze the nitrile group proceded with concomitant isomerization of the (*Z*)-double bond at C-4 to give more stable (*E*)-isomer and also with conjugation of the two double bonds.



Scheme 2. Further unsuccessful attempts to prepare **3**. Reagents: (a) TsCl, C_5H_5N, DMAP (87%); (b) KCN, DMSO [quant. (77% purity)]; (c) NaOH, EtOH, H_2O, reflux, 6 h (87%), (d) CH_2N_2, Et_2O {80% [44% of **15**, 20% of (4*E*,7*Z*)-isomer, 28% of other isomers of **15** and 5% of dihydro compounds]}; (e) $KN(SiMe_3)_2$, PhSeCl,THF (48%); (f) $NaIO_4$, THF, H_2O [45% (61% of **5**, 3% of **3** and other isomers)]; (g) DMP, CH_2Cl_2; (h) TMSC≡CH, MeMgBr, THF; (i) K_2CO_3, MeOH (37%, three steps); (j) $MeC(OMe)_3$, $EtCO_2H$, *o*-xylene, 145°C (1 h) and then 160−170°C (1 h) (85%); (k) Al_2O_3 (basic Brockmann 1), *o*-xylene, 160°C (2 h) [41% (38% of **3**, 21% of **19** and total 25% of isomers of **3** with strong M^+ at m/z = 180)].

Subsequent phenylselenenylation of **15** gave crude **16**, whose oxidative elimination with $NaIO_4$ afforded the desired (2*E*.4*Z*,7*Z*)-**3** only as a minor product (3% of the whole products), while the major product (61% of the whole products) was (2*E*,4*E*,7*Z*)-**5** generated by further isomerization of the double bond at C-4. It therefore became clear that the organoselenium route was inadequate for the synthesis of (2*E*,4*Z*,7*Z*)-**3** due to unexpectedly facile isomerization of the trienoate system of **3**.

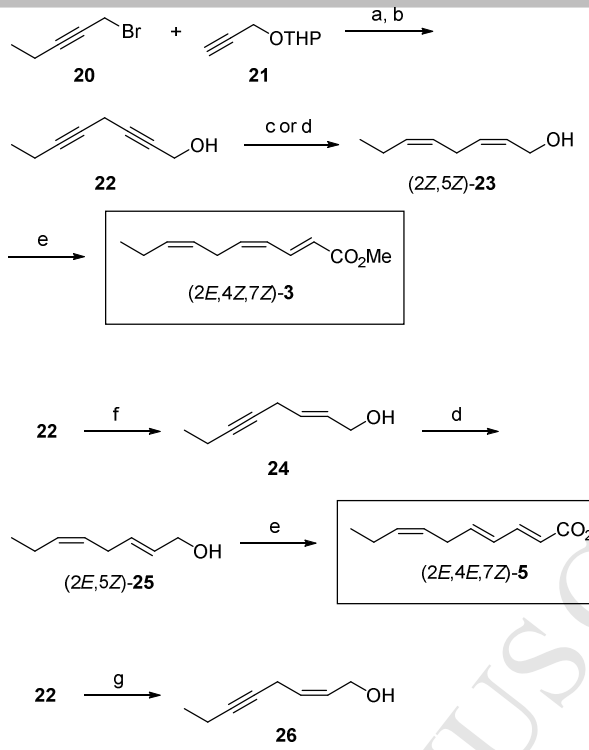
In my previous synthesis of (2*E*,4*Z*)-**2**,[3] methyl 3,4-decadienoate was subjected to Tsuboi's interesting allene to conjugated diene rearrangement reaction[13] to give the desired **2**. The rearrangement was thought to be applicable to the synthesis of (2*E*,4*Z*,7*Z*)-**3** from allene **19**, which could be prepared from commercially available (*Z*)-3-hexen-1-ol (**17**) via acetylenic alcohol **18**. The alcohol **18** was synthesized by ethynylation of (*Z*)-3-hexenal, which was obtained by oxidation of **17** with Dess-Martin periodinane (DMP).[14] Conversion of **18** to **19** was executed via orthoester Claisen rearrangement employing methyl orthoacetate in the presence of propanoic acid. Thermal rearrangement of allene **19** in the presence of Al_2O_3 indeed gave (2*E*,4*Z*,7*Z*)-**3**, but its purity was only 38% with recovered allene **19** (21%) and many other isomers of **3**. It therefore became clear that a new route to **3** must be explored.

2.3. Successful synthesis of methyl (2*E*,4*Z*,7*Z*)-decatrienoate (3) and its (2*E*,4*E*,7*Z*)-isomer (5)

A lesson learned from the failures as described above in 2.2. was the instability of the 2*E*,4*Z*,7*Z*-triene system of **3**. To avoid isomerization of the double bond geometries, the following two points seemed to be of importance: (i) preparation of pure (2*Z*,5*Z*)-2,5-octadien-1-ol (**23**) and (ii) its one-pot conversion to (2*E*,4*Z*,7*Z*)-**3** by a tandem oxidation/olefination process.

The starting material for the synthesis of **3 (Scheme 3)** was commercially available 1-bromo-2-pentyne (**20**). Alkylation of the tetrahydropyranyl (THP) ether (**21**) of propargyl alcohol with **20** was executed as reported by Kobayashi et al. to give 2,5-octadiyn-1-ol (**22**) in 90% yield after deprotection.[15]

Reduction of **22** to (2*Z*,5*Z*)-2,5-octadien-1-ol (**23**) was then examined by employing various different methods. Semi-hydrogenation of **22** to **23** was very sluggish when Lindlar catalyst[16] was employed in either hexane/THF or MeOH. Recently reported Kaneda's Pd/SiO_2-DMSO catalyst[17] in hexane/THF did not work either (extremely sluggish rate of hydrogenation). When Cram's $Pd/BaSO_4$ catalyst was employed in MeOH containing quinoline,[10] hydrogenation took place smoothly at 0−5°C. The course of hydrogenation could be monitored by GC-MS. Hydrogenation of the C-2 triple bond was almost four times more rapid than that of the C-5 triple bond, and the desired (2*Z*,5*Z*)-**23** was generated subsequently. The *Z*/*E* selectivity, however, was not so high, giving 86% pure (2*Z*,5*Z*)-**23** in 87% yield after distillation A number of by-products (*Z*/*E*-isomers and over-reduced alken-1-ols) were present in the distilled product, (2*E*,5*Z*)-isomer having been the major one (6.3%) as analyzed by GC-MS. The selectivity was worse when the hydrogenation was carried out at room temperature (20−22°C), while no hydrogen uptake was observed at −78°C.



Scheme 3. Synthesis of **3** and **5**. Reagents: (a) EtMgBr, CuI, THF; (b) aq. HCl, MeOH (90%, two steps); (c) H_2, Pd/$BaSO_4$, quinoline, MeOH [87% (86% purity)]; (d) Zn, $Br(CH_2)_2Br$, CuBr, LiBr, EtOH, 100 °C (5−6 h), 80°C (16 h for **23** and 3 d for **25**) [70% (99% purity) for (2*Z*,5*Z*)-**23** and 73% (98% purity) for (2*E*,5*Z*)-**25**]; (e) DMP, $Ph_3P{=}CHCO_2Me$, $PhCO_2H$, DMSO, CH_2Cl_2 [71% (85% purity) for **3** and 62% (75% purity) for **5**]; (f) $LiAlH_4$, THF (15%); (g) Zn, $Br(CH_2)_2Br$, EtOH, 100°C (45 min) [50% (96.5% purity)].

Chemical reduction of **22** to **23** was also examined. Titanium (II)-based reduction as reported by Kitching[18] was not suitable for gram-scale preparation. Finally, the best reduction method was found to be the classical one with Zn and EtOH as reported by Brandsma.[19] When Zn activated with $Br(CH_2)_2Br$ was used in EtOH, **22** was reduced to give (*Z*)-2-octen-5-yn-1-ol (**26**) after refluxing for 45 min. Prolonged heating did not reduce the enyne **26** to **23**. However, when Zn activated with $Br(CH_2)_2Br$ in hot EtOH was treated with CuBr and LiBr, the resulting Zn/Cu in EtOH [100°C (bath temperature) for 6 h and 80°C (bath temperature) for 16 h] converted **22** to (2*Z*,5*Z*)-**23** of 99% purity in 70% yield after distillation. It thus became possible to obtain 99% pure (2*Z*,5*Z*)-**23** in gram scale. Chemical reduction with Zn/Cu in EtOH was better in selectivity than catalytic semi-hydrogenation over Pd/$BaSO_4$ catalyst in this particular case.

The final step was the tandem oxidation/olefination to convert (2*Z*,5*Z*)-**23** to (2*E*,4*Z*,7*Z*)-**3**. Tandem MnO_2 oxidation/Wittig olefination as reported by Taylor[20] was first applied to **23**. Unfortunately, however, the product was a messy mixture of unidentified esters. Barrett's DMP oxidation/Wittig olefination method[21] was then examined, and found to be successful. Treatment of (2*Z*,5*Z*)-**23** with Dess-Martin periodinane (DMP) and $Ph_3P{=}CHCO_2Me$ in the presence of $PhCO_2H$

(acceleration catalyst for the Wittig reaction) in CH_2Cl_2/DMSO gave crude (2*E*,4*Z*,7*Z*)-**3** in 71% yield. The overall yield of **3** was 45% based on **20** (four steps). GC-MS analysis of the product revealed it to be a mixture of 85% of (2*E*,4*Z*,7*Z*)-**3**, 6% of the (2*Z*,4*Z*,7*Z*)-isomer, and 2% of the (2*E*,4*E*,7*Z*)-isomer. The product was rechromatographed repeatedly over SiO_2, but the desired ester **3** could not be obtained in pure state. Even after fourth chromatographic purification, the purity remained as 89%. Prof. W. Francke (Hamburg University) informed me that he could obtain pure (2*E*,4*Z*,7*Z*)-**3** after repeated $SiO_2/AgNO_3$ chromatography of my synthetic sample. The IR, ^{1}H NMR and MS spectra of the synthetic (2*E*,4*Z*,7*Z*)-**3** coincided with those of the naturally occurring pheromone component.

Similarly, methyl (2*E*,4*E*,7*Z*)-2,4,7-decatrienoate (**5**) was synthesized as follows. 2,5-Octadiyn-1-ol (**22**) was reduced with lithium aluminum hydride to give (*E*)-2-octen-5-yn-1-ol (**24**). The yield (15%) of this step was quite poor, giving dark polymeric materials as the major products. Reduction of **24** with Zn/Br$(CH_2)_2$Br/CuBr/LiBr in EtOH [100^{o}C (bath temperature) for 5 h and 80^{o}C (bath temperature) for 3 d] gave (2*E*,5*Z*)-**25** (96% purity) in 73% yield. This was subjected to Barrett's tandem DMP oxidation/Wittig olefination to give 75% pure (2*E*,4*E*,7*Z*)-**5** in 62% yield. The overall yield of **5** was 6% based on **17** (five steps). The IR, ^{1}H NMR and MS spectra of the synthetic (2*E*,4*E*,7*Z*)-**5** were consistent with the reported data[5] of the methyl ester **5** derived from the naturally occurring acid **4** isolated from the green alga *Cladophora columbiana*.

2.4. Concise synthesis of (±)-methyl (*E*)-2,4,5-tetradecatrienoate (1)

As to the synthesis of (*R*,*E*)-**1**, the major component, there is a problem due to the instability of the conjugated allene system of **1**. The pheromone **1** was reported to be unstable and readily polymerize with a half-life of about 20 days at −13^{o}C.[2] The final step of the synthesis must therefore employ mild conditions to avoid decomposition of **1**. Of course the synthesis should be as concise as possible.

Landor's first synthesis of (±)-**1** in 1971 was a concise one [Fig. 2 (A)].[6] The known (±)-1-undecyn-3-ol (**27**) yielded (±)-**1** after only five steps, although the yield of the each step was not disclosed in their paper. The conciseness of their approach attracted my attention, because the process might be improved by using contemporary synthetic methods.

Another interesting aspect of Landor's synthesis of (±)-**1** is its modification to obtain optically active **1** starting from the known optically active **27**[3]. Landor and co-workers were the first to find out the reductive elimination of a tetrahydropyranyl(THP)oxy group from 4-(2-tetrahydropyranyloxy)-2-alkyn-1-ols to give allenic 2,3-alkadien-1-ols. They suggested a concerted mechanism via intermediate **A** (Fig. 2).[22-24] If this is the correct mechanism, (*R*)-**28** should afford (*R*)-**29**.

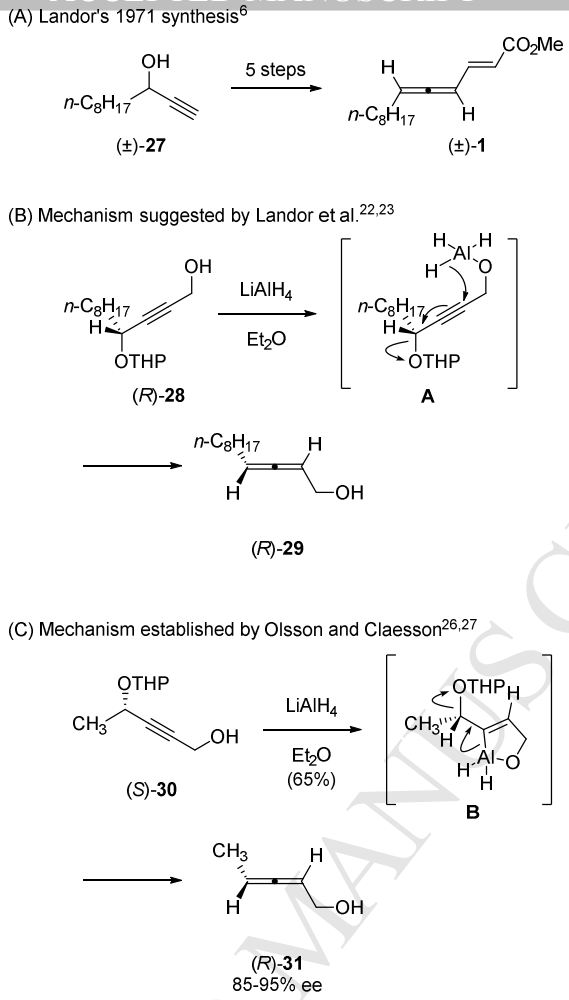
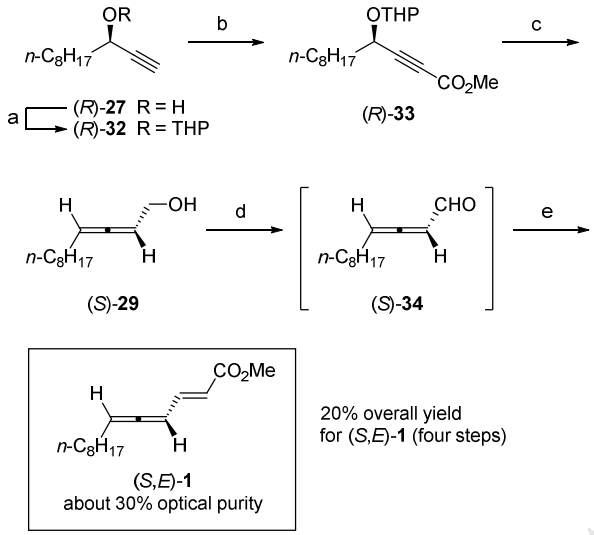


Fig. 2. (A) Landor's 1971 synthesis of (±)-**1** and (B) (C) Proposed mechanisms for conversion of 4-(2-tetrahydropyranyloxy-2-alkyn-1-ols (**28** and **30**) to 2,3-allenic alcohols (**29** and **31**).

A few years later, Olsson and Claesson discovered that (*S*)-**30** gives the known (*R*)-**31** upon reduction with lithium aluminum hydride, and proposed *trans*-hydroalumination/*anti*-elimination mechanism via intermediate **B**.[25,26] Two later works supported the *trans*-addition/*anti*-elimination mechanism.[27,28] Chiral version of Landor's synthesis of (±)-**1** will give an additional opportunity to confirm the mechanism proposed by Olsson and Claesson, because the absolute configurations of optically active **27** and **1** are well-established.[3,29]

The improved synthetic route to **1** is shown in Scheme 4. Methyl 4-(2-tetrahydropyranyloxy)-2-dodecynoate (**33**) was chosen as the substrate for the reduction with lithium aluminum hydride. Accordingly, the known (±)-1-undecyn-3-ol (**27**)[6,29] was treated with 3,4-dihydro-2*H*-pyran (DHP) and *p*-toluenesulfonic acid (TsOH) in diethyl ether to give (±)-**32**, which was converted to the corresponding lithium acetylide by treatment with *n*-butyllithium in THF. Methoxycarbonylation of the acetylide with $ClCO_2Me$ afforded (±)-**33**.



Scheme 4. Synthesis of **1** to provide (±)-**1** and (*S*,*E*)-**1**. [The depicted formulas show the synthesis of (*S*,*E*)-**1**]. Reagents: (a) DHP, TsOH, Et_2O [quant. for both (±)- and (*R*)-**32**]: (b) *n*-BuLi, $ClCO_2Me$, THF [91% for (±)-**33**; 77% for (*R*)-**33**]; (c) $LiAlH_4$, Et_2O [44% for (±)-**29**; 48% for (*S*)-**29**]; (d) DMP, wet CH_2Cl_2 [71% for both (±)- and (*S*)-**34**]; (e) $Ph_3P{=}CHCO_2Me$, CH_2Cl_2 [39-44% for (±)-**1**, 71% for (*S*)-**1** of about 17% optical purity]; (d and e in tandem and one-pot manner[21]) DMP, $Ph_3P{=}CHCO_2Me$, $PhCO_2H$, DMSO, CH_2Cl_2 [27% for (±)-**1** and 54% for (*S*)-**1** of about 30% optical purity].

Reduction of (±)-**33** with lithium aluminum hydride in diethyl ether was followed by chromatographic purification and distillation of the product to give allenic alcohol (±)-**29** in 44% yield. Tandem and one-pot oxidation/Wittig olefination of (±)-**29** was executed by treatment with Dess-Martin periodinane (DMP) and $Ph_3P{=}CHCO_2Me$ in the presence of $PhCO_2H$ in CH_2Cl_2/DMSO.[21] The product was purified by SiO_2 chromatography (twice) to give (±)-**1** in 27% yield. Many by-products were generated at this final stage, including methyl 2,4,6-tetradecatrienoate. Although the overall yield of the present four step-synthesis was only 11% based on (±)-**27**, this synthesis is the shortest one to give (±)-**1**.

The final tandem oxidation/olefination could be executed separately. DMP oxidation of (±)-**29** gave rather unstable (±)-**34** in 71% yield. Its olefination with the Wittig reagent furnished (±)-**1** in 39-44% yield (28-31% yield based on **29**). In this particular case, the tandem procedure did not increase the efficiency of the reactions presumably due to the instability of both (±)-**34** and (±)-**1**.

Synthesis of optically active **1** was then attempted starting from (*R*)-**27**. Preparation of (*R*)-**27** was executed by asymmetric acetylation of (±)-1-trimethylsilyl-1-undecyn-3-ol with vinyl acetate and lipase PS to give its (*R*)-acetate and the recovered (*S*)-alcohol.[3] In 2013, lipase PS coated with an ionic liquid [IL1 : α-cetylpolyoxyethylene(19)ether sulfate] was reported by Itoh and his co-workers to be more active than Amano's commercial lipase PS.[30] Indeed, 250 mg of Itoh's IL l-coated lipase PS was as active as 4.0 g of Amano's lipase PS in effecting the asymmetric acetylation of 4.4 g of the

racemic alcohol under the conditions previously reported (3 days at 30°C).[3] The (*R*)-acetate yields (*R*)-alcohol **27** (97% ee)[3] by treatment with potassium carbonate in methanol and water.[3]

The corresponding THP ether (*R*)-**32**, $[\alpha]_D^{26}$ +103.1 (*c* 3.32, hexane), was treated with *n*-butyllithium and $ClCO_2Me$ to give (*R*)-**33**, $[\alpha]_D^{24}$ +115.4 (*c* 3.40, hexane), in 77% yield. This was reduced with lithium aluminum hydride in diethyl ether to give (+)-**29**, $[\alpha]_D^{23}$ +60.0 (*c* 3.47, hexane), in 48% yield. The absolute configuration of (+)-**29** was determined as *S*, because it gave (*S*,*E*)-**1**. Since (*R*)-**33** afforded (S)-(+)-**29**, the mechanism of the reaction must be as proposed by Olsson and Claesson [Fig. 2 (C)].[25,26]

Finally, tandem oxidation/olefination[21] of (*S*)-**29** furnished (*S*,*E*)-**1** in 54% yield. Its specific rotation, however, was disappointingly small: $[\alpha]_D^{24}$ +45.3 (*c* 1.18, hexane). Because the specific rotation value of (*R*,*E*)-**1** with 87% ee (determined by chiral GC) was $[\alpha]_D^{24}$ −130.3 (*c* 2.23, hexane),[3] the present (*S*,*E*)-**1** was of only 30% optical purity. Extensive racemization must have taken place in the course of the tandem oxidation/olefination process.

The two reactions were then executed separately. DMP oxidation of (*S*)-**29** gave (*S*)-**34**, $[\alpha]_D^{22}$ +21.0 (*c* 1.04, hexane), in 71% yield. Its Wittig olefination furnished (*S*,*E*)-**1** in 71% yield, $[\alpha]_D^{23}$ +25.2 (*c* 1.06, hexane). In this case, the optical purity of (*S*,*E*)-**1** was about 17%. It therefore became clear that the modified Landor process cannot be used for the synthesis of the naturally occurring (*R*,*E*)-**1** (87% ee) due to the racemization in the course of the final oxidation/olefination step probably because of the stereochemical instability of (*S*)-**34**, although the process provides (*S*,*E*)-**1** of about 30% optical purity in 20% overall yield based on (*R*)-**27** (four steps).

The best preparative methods for the racemate and enantiomers of **1** are those in ref. 3.[cf. 31] In the synthesis of (*R*)- and (*S*)-**1**, conditions which may cause racemization are carefully avoided by generating the unstable conjugated allenic ester **1** at the final stage.[3] Gratifyingly, a mixture of our synthetic (*R*,*E*)-**1**[3], **2**[3] and **3** together with other components attracted the dried bean beetles.[4]

3. Conclusions

Synthesis of methyl (2*E*,4*Z*,7*Z*)-2,4,7-decatrienoate (**3**), a new component of the male pheromone of the dried bean beetle (*Acanthoscelides obtectus*), was accomplished by tandem DMP oxidation/Wittig olefination of (2*Z*,5*Z*)-2,5-octadien-1-ol (**23**). Reduction of 2,5-octadiyn-1-ol (**22**) with Zn/Cu in hot EtOH was the best method to secure 99% pure (2*Z*,5*Z*)-**23**. Similarly, methyl (2*E*,4*E*,7*Z*)-2,4,7-decatrienoate (**5**) was synthesized by tandem DMP oxidation/Wittig olefination of (2*E*,5*Z*)-2,5-octadien-1-ol (**25**), which was prepared by reduction of (*E*)-2-octen-5-yn-1-ol (**24**) with Zn/Cu in hot EtOH. Catalytic semi-hydrogenation of **22** was found to be inferior in selectivity to the Zn/Cu reduction in these particular cases.

The modified Landor's method was shown to be a method of choice for preparing (±)-methyl (*E*)-2,4,5-tetradecatrenoate (**1**), the racemate of the major component (*R*,*E*)-**1** of the male pheromone of the dried bean beetle, although the method failed to give optically pure (*S*,*E*)-**1**. Stereochemical

course of the allene formation step was shown to give (*S*)-allene **29** from (*R*)-acetylenic ester **33** in accord with the mechanism proposed by Olsson and Claesson.[25,26]

4. Experimental

4.1. General

Boiling points are uncorrected values. Refractive indices were measured on an Atago EMT-1 refractometer. IR spectra were measured on a Jasco FT/IR-410 spectrometer. ^{1}H NMR spectra (400 MHz, TMS at $\delta = 0.00$ as internal standard) and ^{13}C NMR spectra (100 MHz, $CDCl_3$ at $\delta = 77.0$ as internal standard) were recorded on a Jeol JNM-AL 400 spectrometer. GC-MS were measured on Agilent Technologies 5975 inert XL. HRMS were recorded on Jeol JMS-SX 102A or Waters Synapt G2 HDMS. Column chromatography was carried out on Merck Kieselgel 60 Art 1.07734.

4.2. 2,5-Octadiyn-1-ol (22)

A solution of EtMgBr in Et_2O (TCI, 3 M, 57 mL, 171 mmol) was added dropwise to a stirred solution of **21** (23.8 g, 170 mmol) in dry THF (285 mL) under argon. When the exothermic reaction with evolution of ethane ceased after 30 min at reflux, CuI (2.5 g, 13 mmol) was added to the solution. Subsequently, a solution of **20** (Wako Chemical, 21.5 g, 154 mmol) in dry THF (20 mL) was added dropwise over 30 min. The reaction was exothermic to raise the inner temperature to 45−47^{o}C, and solid $MgBr_2$ separated from the solution. The mixture was stirred overnight, and then concentrated in vacuo to remove Et_2O and THF. The residue was diluted with ice and NH_4Cl solution, and extracted with Et_2O. The Et_2O solution was washed with brine, dried ($MgSO_4$), and concentrated in vacuo to give 36.8 g (quant.) of the THP ether of **22** as an oil, νmax (film): 2941 (s), 2237 (w), 1120 (s), 1025 (s). This oil was dissolved into MeOH (300 mL) containing conc HCl (10 mL), and the solution was stirred for 1 h at room temperature. It was then neutralized with solid $NaHCO_3$, and concentrated in vacuo. The residue was diluted with water, and extracted with Et_2O. The Et_2O solution was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled to give 16.0 g (90%) of **22** as a colorless oil, bp 86−88^{o}C/4 Torr; $n_D^{18} = 1.4951$; νmax (film): 3338 (br. s), 2977 (s), 2938 (m), 2920 (m), 2877 (m), 2259 (w), 1455 (m), 1415 (m), 1320 (s), 1115 (m), 1013 (s); δ_H ($CDCl_3$): 1.13 (3H, t, *J* 7.2), 1.90−2.00 (1H, br.), 2.18 (2H, qt, *J* 7.2, 2.4), 3.19 (2H, m), 4.27 (2H, t, *J* 2.4); GC-MS [column: HP-5MS, 5% phenylmethylsiloxane, 30 m x 0.25 mm i.d., carrier gas, He; press: 60.7 kPa; temp: 70-230^{o}C (+10^{o}C/min)]: t_R 8.18 min (99.0%). MS (70 eV, EI): *m*/*z*: 122 (5) [M^+], 121 (7) [$(M-1)^+$], 107 (18), 104 (79), 91 (69), 79 (40), 78 (38), 77 (100), 65 (30), 51 (24), 39 (26). HRMS calcd for $C_8H_{10}O$: 122.0732, found: 122.0731.

4.3. (2*Z*,5*Z*)-2,5-Octadien-1-ol (23)

4.3.1. By catalytic hydrogenation. 5% Pd/$BaSO_4$ (TCI, 1.15 g) was added to a solution of **22** (3.70 g, 30 mmol) and quinoline (1.0 mL) in MeOH (50 mL). The mixture was stirred vigorously at 0−5°C (ice-water) under H_2 atmosphere (balloon). The H_2 uptake ceased after 3.5 h. The mixture was filtered through Celite, and the Celite layer was washed with Et_2O. The filtrate and washings were concentrated in vacuo, and the residue was dissolved in Et_2O. The Et_2O solution was successively washed with dil HCl, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo to give 3.34 g (87%) of **23**. Distillation of a portion (2.32 g) of it gave 1.62 g of purified **23**, bp 59°C/1 Torr; n_D^{18}=1.4698: νmax (film):3323 (br. s), 3013 (s), 2964 (s), 2933 (s), 2874 (s), 1650 (w), 1462 (m), 1023 (s), 716 (m); δ_H ($CDCl_3$): 0.98 (3H, t, *J* 7.6), 1.40 (1H, br. s), 2.07 (2H, dq, *J* 7.6, 7.6), 2.83 (2H, t, *J* 7.2), 4.24 (2H, br, s); 5.26−5.33 (1H, m), 5.39−5.45 (1H, m), 5.50−5.55 (1H, m), 5.55−5.65 (1H, m), GC-MS (same conditions as those for **22**): t_R 6.09 min (1.1%). 6.19 (1.6%), 6.27 (86.0%, **23**), 6.31 (6.3%), 6.38 (3.3%). MS of (2*Z*,5*Z*)-**23** (70 eV, EI): *m*/*z*: 124 (<1) $[M-2)^+]$, 108 (25), $[M-H_2O)^+]$: 93 (31), 79 (100), 77 (30), 70 (19), 67 (33), 55 (27), 41 (29). HRMS calcd for C_8H_{12} $[(M-H_2O)^+]$: 108.0939, found: 108.0936. Column chromatography over SiO_2 before distillation did not improve the purity of the product.

4.3.2. By reduction with Zn/Cu in EtOH. $Br(CH)_2Br$ (0.8 mL) was added to powdered zinc (Aldrich 209988, 14.0 g, 214 mmol) in anhydrous EtOH (20 mL) under argon. The mixture was stirred and heated under reflux for 10 min. Then $Br(CH_2)_2Br$ (0.8 mL) was added again, and the mixture was stirred and heated under reflux for another 10 min. When the inner temperature dropped to 50°C, CuBr (3.2 g, 22 mmol) and LiBr (4.8 g, 55 mmol) in dry THF (15 mL) were added to the mixture with vigorous stirring. Subsequently, a solution of **22** (4.88 g, 40 mmol) in anhydrous EtOH (10 mL) was added to the mixture, and the stirring and heating were continued for 6 h at 100°C and then 16 h at 80°C under argon. After cooling, the mixture was diluted with NH_4Cl solution and thoroughly extracted with Et_2O. The Et_2O solution was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled to give 3.55 g (70%) of **23** as a colorless oil, bp 64−65°C/4 Torr; GC-MS (same conditions as those for **22**): t_R 6.25 min (98.9%, **23**).

4.4. (*Z*)-2-Octen-5-yn-1-ol (26)

$Br(CH_2)_2Br$ (0.4 mL) was added to powdered zinc (Aldrich 209988, 7.0 g, 107 mmol) in anhydrous EtOH (10 mL) under argon. The mixture was stirred and heated under reflux for 10 min. Then $Br(CH_2)_2Br$ (0.4 mL) was added again and the mixture was stirred and heated under reflux for another 10 min. After cooling to 40°C, a solution of **22** (2.44 g) in anhydrous EtOH (2.5 mL) was added to the mixture, and the stirring and heating were continued for 45 min under reflux. After cooling, the mixture was diluted with NH_4Cl solution and thoroughly extracted with Et_2O. The Et_2O solution was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled to give 1.24 g (50%) of **26** as a colorless oil, bp 78−79°C/3 Torr; n_D^{18}= 1.4822: νmax (film):3349 (br. s), 3026 (m), 2976 (s), 2937 (s), 2878 (s), 1657 (w), 1456 (m), 1422 (m), 1320

(m),1290 (m), 1025 (s), 937 (w); δ_H ($CDCl_3$): 1.11 (3H, t, *J* 7.2), 1.60−1.82 (1H, br.), 2.12−2.19 (2H, m), 2.94−2.96 (2H, m), 4.22 (2H, d, *J* 5.2), 5.56−5.62 (1H, m), 5.64−5.70 (2H, m); GC-MS (same conditions as those for **22**): t_R 7.14 min (96.5%). MS (70 eV, EI): *m*/*z*: 123 (2) [$(M-1)^+$], 106 (47), [$(M-H_2O)^+$], 95 (30), 91 (100), 79 (40), 78 (29), 77 (43), 70 (28), 65 (23), 57 (13), 53 (16), 41 (21), 39 (25), HRMS calcd for C_8H_{10} [$(M-H_2O)^+$]: 106.0785, found: 106.0785.

4.5. Methyl (2*E*,4*Z*,7*Z*)-2,4,7-decatrienoate (3)

DMP (1.106 g, 2.6 mmol) was added in one portion to a stirred and ice-cooled solution of (2Z,5Z)-**23** (98.9% purity, 259 mg, 2 mmol), $PhCO_2H$ (490 mg, 4 mmol), $Ph_3P=CHCO_2Me$ (1.39 g, 4 mmol) and DMSO (1.5 mL) in CH_2Cl_2 (7.5 mL) at 0−5°C. The ice-bath was removed after the addition, and the mixture was stirred for 30 min at room temperature. The colorless mixture soon turned yellow, and then darkened to give a dark red solution. It was cooled again at 0−5°C, and saturated $NaHCO_3$ solution (30 mL) was added to the mixture. After stirring for 1 h, the mixture was diluted with Et_2O and filtered through Celite. The Celite layer was washed with Et_2O. The combined filtrate and washings were washed with brine, dried ($MgSO_4$), and concentrated in vacuo to give 0.3 g of a dark oil. This was chromatographed over SiO_2 (15 g). Elution with hexane/EtOAc (75 : 1) gave 264 mg (71%) of 85% pure (2*E*,4*Z*,7*Z*)-**3** as a colorless oil, n_D^{18}=1.5060: νmax (film):3012 (m), 2964 (m), 2875 (m), 1721 (vs), 1638 (s), 1604 (m), 1435 (s), 1407 (m), 1311 (m),1268 (s), 1204 (m), 1170 (s), 1133 (m), 995 (m), 869 (m), 727 (m), 705 (m); δ_H ($CDCl_3$): 0.99 (3H, t, *J* 7.2), 2.09 (2H, dq, *J* 7.2, 7.2), 3.05 (2H, dd-like, *J* 7.2, 7.2), 3.76 (3H, s), 5.32 (1H, dt, *J* 10, 7), 5.45 (1H, dt *J* 10, 7), 5.80 (1H, dt, *J* 11, 7.6), 5.89 (1H, d, *J* 15), 6.13 (1H, dd, *J* 7, 7), 7.65 (1H, dd, *J* 15, 10); δ_C ($CDCl_3$): 14.1, 20.5, 26.4, 51.5, 121.0, 125.0, 126.3, 133.2, 139.35, 139.37, 167.6; GC-MS (same conditions as those for **22**): t_R 10.88 min [85.1%, (2*E*,4*Z*,7*Z*)-**3**], .10.98 [6.0%, (2*Z*,4*Z*,7*Z*)-isomer], 11.36 [2.1%, (2*E*,4*E*,7*Z*)-isomer]. MS of **3** (70 eV, EI): *m*/*z*: 180 (5) [M^+], 165 (2), 149 (14), 137 (16), 121 (53), 120 (38), 119 (36), 111 (55), 105 (40), 98 (28), 93 (34), 91 (88), 79 (100), 77 (46), 67 (21), 65 (20), 55 (29), 39 (22). The MS was identical with that of the naturally occurring pheromone component. HRMS calcd for $C_{11}H_{16}O_2$: 180.1150, found: 180.1158. Attempted purification of **3** by repeated chromatography over SiO_2 was fruitless. The purest **3** obtained was 89.1% pure with 6.2% of (2*Z*,4*Z*,7*Z*)- and 1.7% of (2*E*,4*E*.7*Z*)-isomers.

4.6. (*E*)-2-Octen-5-yn-1-ol (24)

A solution of **22** (3.66 g, 30 mmol) in dry THF (10 mL) was added dropwise to a stirred and ice-cooled suspension of $LiAlH_4$ (1.36 g, 36 mmol) in dry THF (20 mL) at 5−10°C. The mixture was stirred for 3 h with ice-cooling. It gradually darkened in color. The reaction was then quenched by slow addition of water with ice-cooling. Subsequently, the mixture was poured into ice and dil HCl containing NH_4Cl, and extracted with Et_2O. The Et_2O solution was successively washed with water, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo. The dark-colored residual

oil was chromatographed over SiO_2 (40 g). Elution with hexane/EtOAc (10 : 1) gave 1.11 g of **24** as an oil. This was distilled to give 552 mg (15%) of pure **24** as a colorless oil, bp 85−87°C/4 Torr; n_D^{19}=1.4850: ν max (film):3333 (br. s), 2976 (s), 2937 (s), 2918 (s), 2878 (s), 1672 (w), 1456 (m), 1421 (m), 1322 (m), 1094 (m), 997 (s), 971 (s); δ_H ($CDCl_3$): 1.14 (3H, t, *J* 7.6), 1.52 (1H, br), 2.17−2.23 (2H, m), 2.95 (2H, br, s-like), 4.15 (2H, br. s-like), 5.68−5.74 (1H, m), 5.88−5.94 (1H, m); GC-MS (same conditions as those for **22**): t_R 7.39 min (93.0%, **24**). MS (70 eV, EI): *m*/*z*: 123 (4) [$(M-1)^+$], 109 (30), 95 (75), 91 (69), 79 (100), 77 (75), 67 (34), 65 (30), 57 (37), 53 (23), 41 (27), 39 (32). HRMS calcd for $C_8H_{12}O$: 124.0888, found: 124.0882.

4.7. (2*E*,5*Z*)-2.5-Octadien-1-ol (25)

$Br(CH_2)_2Br$ (0.1 mL) was added to powdered zinc (Aldrich 209988, 2.0 g, 31 mmol) in anhydrous EtOH (3 mL) under argon. The mixture was stirred and heated under reflux for 10 min. Then $Br(CH_2)_2Br$ (0.1 mL) was added again, and the mixture was stirred and heated under reflux for another 10 min. After cooling to 50°C, a mixture of CuBr (0.3 g, 2 mmol) and LiBr (0.5 g, 6 mmol) in dry THF (2 mL) was added to the mixture with vigorous stirring. Subsequently, a solution of **24** (310 mg, 2.5 mmol) in anhydrous EtOH (2 mL) was added to the mixture, and the stirring and heating were continued for 5 h at 100°C and then 3 d for 80°C. After cooling, the mixture was diluted with NH_4Cl solution and thoroughly extracted with Et_2O. The Et_2O solution was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to give 245 mg (73%) of (2*E*,5*Z*)-**25** as a colorless oil, n_D^{20}=1.4733: ν max (film):3334 (br. s), 3010 (m), 2963 (s), 2932 (s), 2837 (s), 1668 (w), 1461 (m), 1090 (m), 1005 (s), 970 (s); δ_H ($CDCl_3$): 0.97 (3H, t *J* 7.6), 1.21 (1H, br. s), 2.05 (2H, dt, *J* 7.2, 7.6), 2.92 (2H, t-like, *J* 6.4), 3.74 (2H, br. s), 5.36 (1H, dt, *J* 10.8, 7.2), 5.50 (1H, dt, *J* 10.8, 7.2), 5.80 (1H, d, *J* 15.6), 6.14 (1H, dt, *J* 15.6, 6.8); GC-MS (same conditions as those for **22**): t_R 6.31 min (98.4%, **25**). MS (70 eV, EI): *m*/*z*: 126 (<1) [M^+], 108 (20), 98 (12), 95 (36), 93 (39), 91 (31), 84 (54), 83 (49), 82 (43), 79 (80), 77 (47), 70 (27), 67 (100), 57 (42), 55 (81), 53 (27), 51 (13), 43 (19), 41 (76), 39 (46), 31 (12). HRMS calcd for $C_8H_{14}O$: 126.1045, found: 126.1047.

4.8. Methyl (2*E*,4*E*,7*Z*)-2,4,7-decatrienoate (5)

DMP (1.206 g, 2.8 mmol) was added in one portion to a stirred and ice-cooled solution of (2*E*,5*Z*)-**25** (237 mg, 2 mmol), $PhCO_2H$ (492 mg, 4 mmol), $Ph_3P{=}CHCO_2Me$ (1.39 g, 4 mmol) and DMSO (1.5 mL) in CH_2Cl_2 (7.5 mL) at 0−5°C. After stirring for 30 min at room temperature, the mixture was worked up as described for **3** in 4.5 to give 208 mg (62%) of 75.6% pure (2*E*,4*E*,7*Z*)-**5**, n_D^{16}=1.5127; ν max (film):3014 (m), 2962 (s), 2935 (m), 2875 (m), 1720 (vs), 1641 (s), 1617 (m), 1435 (m), 1267 (s), 1203 (m), 1171 (m), 1138 (s), 1002 (m), 866 (w), 714 (m); δ_H ($CDCl_3$): 0.97 (3H, t, *J* 7.6), 2.04 (2H, quint-like *J* 6.4), 2.91 (2H, t, *J* 6.8), 3.74 (3H, s), 5.36 (1H, dt *J* 10.8, 6.8), 5.50 (1H, dt, *J* 10.8, 6.8), 5.80 (1H, d, *J* 15.6), 6.12 (1H, dt, *J* 15.6, 9.2), 6.16 (1H, dt, *J* 15.6, 10.8), 7.27 (1H, dd, *J* 10.8, 16.2); δ_C ($CDCl_3$): 14.1, 20.5, 30.5, 51.4, 119.0, 124.4, 128.2, 133.8, 142.5, 145.0, 167.7;

GC-MS (same conditions as those for **22**): t_R 10.69 min (4.4%, M^+ = 180, isomer of **5**), 11.14 (9.2%, strong M^+ at 180, unidentified), 11.32 [6.9%, M^+ =180, (2*Z*,4*E*,7*Z*)-isomer], 11.38 (75.6%, **5**), 11.62 (1.4%, strong M^+ at 180, unidentified). MS of **5** (70eV, EI): m/z: 180 (12) [M^+], 149 (17), 138 (14), 137 (9), 133 (8), 124 (14), 121 (44), 120 (35), 119 (42), 111 (72), 105 (37), 98 (44), 93 (32), 91 (81), 81 (32), 79 (100), 77 (44), 68 (21), 67 (22), 66 (17), 65 (21), 59 (23), 55 (35), 53 (21), 39 (26). These IR, ^{1}H NMR and MS data are in good accord with the reported data.[5] HRMS calcd for $C_{11}H_{16}O_2$: 180.1150, found: 180.1148.

4.9. 1-Undecyn-3-ol THP ether (32)

4.9.1. Racemate. TsOH·H_2O (200 mg, 1.2 mmol) was added to a solution of (±)-**27** (6.0 g, 35.7 mmol) and DHP (3.8 g, 45 mmol) in dry Et_2O (60 mL) with shaking in an ice-bath. After the initial exothermic reaction, the mixture was left to stand for 3 h at room temperature. It was then diluted with Et_2O, washed with aqueous K_2CO_3 solution and brine, dried ($MgSO_4$), and concentrated in vacuo to give 9.2 g (quant.) of (±)-**32** as a colorless oil, n_D^{25}=1.4544; IR νmax (film) cm^{-1}: 3310 (m), 2926 (s), 2855 (s), 2111 (w), 1467 (m), 1455 (m), 1201 (m), 1118 (s), 1077 (m), 1022 (s), 974 (m), 871 (m), 656 (m), 625 (m); Different batches of (±)-**32** showed different ^{1}H NMR spectra due to their differences in diastereomeric ratios originating from the stereogenic center in THP: δ_H ($CDCl_3$): 0.88 (3H, t, *J* 7.2), 1.27 (8H, br. s), 1.40−1.65 (7H, m), 1.65−1.90 (5H, m), 2.368 (0.8H, d, *J* 2), 2.426 (0.2H, d, *J*2), 3.50−3.56 (1H, m), 3.81 (0.8H, m), 4.02 (0.2H, m), 4.38 (0.2H, m), 4.41 (0.8H, m), 4.75 (0.2H, t, *J* 3.2), 4.98 (0.8H, t, *J* 3.2). HRMS calcd for $C_{16}H_{28}O_2Na$ [$(M+Na)^+$]: 275.19815, found: 275.1981.

4.9.2. (R)-Isomer. Similarly, (*R*)-**27** {2.10 g; $[\alpha]_D^{25}$+13.8 (*c* 4.01, Et_2O)} yielded 3.34 g (quant.) of (*R*)-**32** as an oil, n_D^{26}=1.4546; $[\alpha]_D^{26}$+103.1 (*c* 3.32, hexane). Its IR and ^{1}H NMR spectra were identical with those of (±)-**32**.

4.10. Methyl 4-(2-tetrahydropyranyloxy)-2-dodecynoate (33)

4.10.1. Racemate. A solution of *n*-BuLi in hexane (1.6 M, 23.2 mL, 37 mmol) was added dropwise to a stirred and cooled solution of (±)-**32** (9.22 g, 36.6 mmol) in dry THF (30 mL) at −78 to −60°C under argon. The slightly yellowish mixture was warmed to −15°C and then cooled again at −70°C. A solution of $ClCO_2Me$ (3.78 g, 40 mmol) in dry THF (10 mL) was added dropwise to the stirred and cooled mixture. The mixture was stirred for 1 h at −78°C and an additional 1 h at room temperature until the colorless precipitates of LiCl separated. It was then quenched with aqueous NH_4Cl solution, and extracted with Et_2O. The Et_2O solution was washed successively with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue (12.5 g) was chromatographed over SiO_2 (100 g). Elution with hexane/EtOAc (50:1) gave 10.4 g (91%) of (±)-**33** as a colorless oil, n_D^{26}=1.4612; νmax (film): 2927 (s), 2855 (s), 2235 (m), 1720 (s), 1456 (m), 1435 (m), 1252 (s), 1119 (m), 1022 (s), 973 (m), 751 (m). Different batches of (±)-**33** showed different ^{1}H NMR spectra due to their differences in diastereomeric composition originating from the stereogenic center in THP. In one occasion the

^{1}H NMR spectrum of a single diastereomer of (±)-**33** was observed: δ_H ($CDCl_3$): 0.88 (3H, t, *J* 6.8), 1.21−1.35 (10H, br), 1.40−1.50 (2H, m), 1.50−1.70 (5H, m), 1.70−1.90 (3H, m), 3.52−3.60 (1H, m), 3.77 (3H, s), 3.95−4.03 (1H, m), 4.34 (1H, t, *J* 6.8), 4.75 (1H, t, *J* 3.2). Another diastereomer showed the following signals: δ_H ($CDCl_3$): 3.78 (3H, s, CO_2CH_3), 4.53 (1H, t, *J* 6.8), 4.92 (1H, t, *J* 3.2); GC−MS (same conditions as those for **22**): t_R 18.91 min [0.84%, a diastereomer of (±)-**33**],19.18 min [98.69%, another diastereomer of (±)-**33**]. These two diastereomers showed slightly different MS. MS(70 eV, EI) of (±)-**33** with t_R 18.91 min: *m*/*z*: 309 (<1) [M^+−1], 210 (14), 209 (100) [M^+−THPO], 177 (8), 149 (14), 107 (12), 93 (14), 85 (87) [THP], 79 (13), 67 (11), 55 (12), 41 (12); MS (70 eV, EI) of (±)-**33** with t_R 19.18 min: *m*/*z*: 309 (<1) [M^+−1], 210 (9), 209 (59), 177 (4), 149 (6), 114 (10), 107 (7), 93 (10), 85 (100), 79 (14), 67 (10), 55 (15), 41 (14). HRMS calcd for $C_{18}H_{30}O_4Na$ [$(M+Na)^+$]: 333.2036, found: 333.2035.

4.10.2. (R)-Isomer. Similarly, (*R*)−**32** (3.30 g) furnished 3.12 g (77%) of (*R*)-**33** as an oil, n_D^{24}=1.4628; $[\alpha]_D^{24}$+115.4 (*c* 3.40, hexane); GC−MS (same conditions as for **22**): t_R 18.93 min (87.6%), 19.10 min (13.4%). Its IR, ^{1}H NMR and MS spectra were identical with those of (±)-**33**.

4.11 2,3-Dodecadien-1-ol (29)

4.11.1. Racemate. A solution of (±)-**33** (10.3 g, 33 mmol) in dry Et_2O (10 mL) was added dropwise to the stirred and ice-cooled suspension of $LiAlH_4$ (2.3 g, 60 mmol) in dry Et_2O (80 mL) at 5−15^{o}C. After the addition, the mixture was stirred and heated under reflux for 2 h. After cooling, the excess $LiAlH_4$ was destroyed by successive addition of water (2 mL), 15% aqueous NaOH solution (2 mL), and water (6 mL) to the stirred and ice-cooled reaction mixture. The mixture was stirred for 30 min at room temperature, and filtered through Celite. The Celite layer was washed with Et_2O. The combined filtrate and washings were dried ($MgSO_4$), and concentrated. The residue (4.0 g) was chromatographed over SiO_2 (80 g). Elution with hexane gave 0.83 g of hydrocarbons, and further elution with hexane/EtOAc (50:1) gave 2.66 g (44%) of (±)-**29**, bp 104^{o}C/2 Torr, n_D^{26}=1.4712; νmax (film): 3325 (m, br), 2955 (s), 2925 (s), 2854 (s), 1964 (w), 1465 (m), 1013 (m), 870 (w), 722 (w); δ_H ($CDCl_3$): 0.88 (3H, t, *J* 7.2), 1.27 (10H, br. s), 1.40 (2H, dt, *J* 7.2, 6.8), 1.52 (1H, br.), 1.99−2.05 (2H, m), 4.11 (2H, dd, *J* 7.2, 5.6), 5.26−5.36 (2H, m); GC−MS (same conditions as those for **22**): t_R 11.97 min (96.8%), MS (70 eV, EI): *m*/*z*: 180 (<1) [M^+], 164 (1), 151 (1), 135 (4), 121 (6), 107 (8), 95 (14), 93 (16), 91 (13), 84 (86), 83 (90), 79 (40), 69 (43), 67 (40), 56 (60), 55 (100), 43 (40), 41 (52). HRMS calcd for $C_{12}H_{22}O$: 182.1671, found: 182.1684.

4.11.2. (S)-Isomer. Similarly, 3.10 g (10 mmol) of (*R*)-**33** was reduced with 0.76 g (20 mmol) of $LiAlH_4$ in Et_2O (35 mL) to give 878 mg (48%) of (*S*)-**29** as a colorless oil, n_D^{23}=1,4708; $[\alpha]_D^{23}$+60.0 (*c* 3.47, hexane). Its IR, ^{1}H NMR and MS spectra were identical with those of (±)-**29**, GC-MS (same conditions as those for **22**): t_R 11.95 min (98.7%).

4.12. 2,3-Dodecadienal (34)

4.12.1 Racemate. DMP (870 mg, 2.1 mmol) was added portionwise to a stirred and

ice-cooled solution of (±)-**29** (259 mg, 1.4 mmol) in CH_2Cl_2 (6 mL) containing H_2O (32 mg). After 5 min, the ice-bath was removed, and the mixture was stirred for 1 h at room temperature to give a colorless suspension of *o*-iodobenzoic acid. The reaction was quenched by adding Et_2O and aqueous $NaHCO_3$ solution. The mixture was then filtered through Celite, and the Celite layer was washed with Et_2O. The Et_2O solution was separated from the aqueous filtrate, washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed over SiO_2 (4 g). Elution with hexane/EtOAc (50:1) gave (±)-**34** (184 mg, 71%) as a colorless oil, n_D^{21}=1.4778; νmax (film): 2926 (s), 2855 (s), 2720 (w), 1944 (m), 1692 (s), 1465 (m), 1168 (m), 1081 (m), 878 (m), 456 (m); δ_H ($CDCl_3$): 0.88 (3H, t, *J* 7.2), 1.28 (10H, br. s), 1.47 (2H, dt, *J* 7.6, 7.2), 1.55 (1H, br. s), 2.15−2.22 (2H, m), 5.72−5.77 (1H, m), 5.78−5.83 (1H, m), 9.48 (1H, d, *J* 3.2); GC−MS (same conditions as those for **22**): t_R 11.71 min (88.6%); MS (70eV, EI): *m*/*z*: 180 (5) [M^+], 151 (2), 137 (7), 123 (23), 109 (13), 95 (31), 83 (42), 81 (100), 67 (23), 55 (27), 41 (32). This aldehyde was unstable and no good HRMS data could be collected.

4.12.2. (S)-Isomer. Similarly, 583 mg (3.2 mmol) of (*S*)-**29** was oxidizded with 2.40 g (5.66 mmol) of DMP to give 410 mg (71%) of (*S*)-**34** as a colorless oil, n_D^{23}=1,4771; $[\alpha]_D^{22}$+21.0 (*c* 1.04, hexane). Its IR, ^{1}H NMR and MS spectra were identical with those of (±)-**34**.

4.13. Methyl (*E*)-2,4,5-tetradecatrienoate (1)

4.13.1. Racemate. (a) Tandem DMP oxidation/Wittig reaction. DMP (1.106 g, 2.6 mmol) was added over 3 min to a stirred and ice-cooled solution of (±)-**29** (364 mg, 2 mmol), $PhCO_2H$ (490 mg, 4 mmol) and $Ph_3P{=}CHCO_2Me$ (1.385 g, 4 mmol) in CH_2Cl_2 (7.5 mL) and DMSO (1.5 mL) containing a drop of H_2O. The mixture was then stirred for 30 min at room temperature. Subsequently, the mixture was diluted with aqueous $NaHCO_3$ solution (30 mL), stirred for 30 min, and filtered through Celite. The Celite layer was washed with Et_2O. The Et_2O solution was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The brown residue (1.4 g) was chromatographed over SiO_2 (20 g). Elution with hexane/EtOAc (50:1) gave 277 mg of crude (±)-**1**. This was rechromatographed over SiO_2 (7 g). Elution with hexane/EtOAc (50:1) gave 130 mg (27%) of (±)-**1** as the first fraction, and 29 mg of the second fraction containing methyl 2,4,6-tetradecatrienoate (tentative) and (±)-**1**. In another run, the yield was 118 mg (25%). Properties of (±)-**1** as a slightly yellowish oil: n_D^{25}=1.4910, νmax (film): 2926 (s), 2855 (s), 1943 (m), 1721 (s), 1630 (m), 1437 (m), 1306 (m), 1264 (m), 1242 (m), 1176 (m), 1139 (m), 984 (m), 882 (w), 858 (w); δ_H ($CDCl_3$): 0.88 (3H, t, *J* 6.8), 1.22−1.36 (10H, br), 1.36−1.50 (2H, m), 2.02−2.10 (2H, m), 3.74 (3H, s), 5.44 (1H, q, *J* 6.8), 5.85 (1H, dd, *J* 0.7, 15), 5.86−5.92 (1H, m), 7.14−7.26 (1H, m); GC−MS (same condition as those for **22**): t_R 15.91 min (78.0%); MS (70 eV, EI) of (±)-**1** : *m*/*z*: 236 (<1) [M^+], 138 (52), 137 (28), 123 (13), 107 (25), 106 (23), 105 (21), 91 (25), 79 (100), 78 (35), 77 (22), 67 (14), 55 (11), 41 (16). HRMS calcd for $C_{15}H_{24}O_2$: 236.1776, found: 236.1782. *(b) Wittig reaction with (±)-***34**. The stabilized ylid $Ph_3P{=}CHCO_2Me$ (501 mg, 1.5 mmol) was added to a solution of (±)-**34** (189 mg, 1.04 mmol) in dry CH_2Cl_2 (4 mL), and the mixture was stirred for 1.5 h at room temperature under argon. The yellowish solution was concentrated, and the residue was triturated with hexane/Et_2O. The hexane/Et_2O solution was

separated from solid Ph_3PO, and chromatographed over SiO_2 (5 g). Elution with hexane/EtOAc (50:1) gave 109 mg (44%) of (±)-**1**. In another run, the yield was 39%. Its spectral properties were identical with those described above for (±)-**1**.

4.13.2. (S)-Isomer. (a) Tandem DMP oxidation/Wittig reaction. Similarly, 182 mg (1 mmol) of (*S*)-**29** was treated with DMP (700 mg, 1.65 mmol), $PhCO_2H$ (224 mg, 2 mmol) and $Ph_3P{=}CHCO_2Me$ (668 mg, 2 mmol) to give 128 mg (54%) of (*S*)-**1** as a yellowish oil, n_D^{23}=1.4900, $[\alpha]_D^{24}$ +45.3 (*c* 1.18, hexane){about 30% optical purity, because (*R*)-**1** of 87% ee showed $[\alpha]_D^{24}$−130.3 (*c* 2.23, hexane)}[3] Its IR, ^{1}H NMR and MS spectra were identical with those of (±)-**1**. *(b) Wittig reaction with (S)*-**34**. Similarly, 281 mg (1.56 mmol) of (*S*)-**34** and 1.00 g (3 mmol) of $Ph_3P{=}CHCO_2Me$ with 360 mg (3 mmol) of $PhCO_2H$ in CH_2Cl_2 (6 mL) gave 260 mg (71%) of (*S*)-**1** as a yellowish oil, n_D^{22}=1.4933; $[\alpha]_D^{23}$+25.2 (*c* 1.06, hexane) (about 17% optical purity). Its IR, ^{1}H NMR and MS spectra were identical with those of (±)-**1**.

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Supplementary data

Supplementary data describing the experimental details of the unsuccessful routes shown in Schemes 1 and 2 can be found in the online version of this article at doi: 10.1016/j. tet. 2015.00.000.

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Legends for Figures and Schemes

Fig. 1. Structures **1**, **2** and **3** of the pheromone components of the male dried bean beetle, *Acanthoscelides obtectus*, and structure **4** of a metabolite of the green alga, *Cladophora columbiana*.

Fig. 2. (A) Landor's 1971 synthesis of (±)-**1** and (B) (C) Proposed mechanisms for conversion of 4-(2-tetrahydropyranyloxy-2-alkyn-1-ols (**28** and **30**) to 2,3-allenic alcohols (**29** and **31**).

Scheme 1. Attempts to prepare **2** and **3** via organopalladium chemistry. Reagents: (a) $PdCl_2(Ph_3P)_2$, CuI, Et_3N, THF (50% for **8**); (b) H_2, $Pd/BaSO_4$, quinolone, MeOH (45%); (c) I_2, morpholine, C_6H_6 (27%); (d) $Pd(OAc)_2$, K_2CO_3, $(n\text{-}Bu)_4NCl$, DMF.

Scheme 2. Further unsuccessful attempts to prepare **3**. Reagents: (a) TsCl, C_5H_5N, DMAP (87%); (b) KCN, DMSO [quant. (77% purity)]; (c) NaOH, EtOH, H_2O, reflux, 6 h (87%), (d) CH_2N_2, Et_2O {80% [44% of **15**, 20% of (4*E*,7*Z*)-isomer, 28% of other isomers of **15** and 5% of dihydro compounds]}; (e) $KN(SiMe_3)_2$, PhSeCl,THF (48%); (f) $NaIO_4$, THF, H_2O [45% (61% of **5**, 3% of **3** and other isomers)]; (g) DMP, CH_2Cl_2; (h) TMSC≡CH, MeMgBr, THF; (i) K_2CO_3, MeOH (37%, three steps); (j) $MeC(OMe)_3$, $EtCO_2H$, *o*-xylene, 145°C (1 h) and then 160−170°C (1 h) (85%); (k) Al_2O_3 (basic Brockmann 1), *o*-xylene, 160°C (2 h) [41% (38% of **3**, 21% of **19** and total 25% of isomers of **3** with strong M^+ at *m*/*z* = 180)].

Scheme 3. Synthesis of **3** and **5**. Reagents: (a) EtMgBr, CuI, THF; (b) aq. HCl, MeOH (90%, two steps); (c) H_2, Pd/$BaSO_4$, quinoline, MeOH [87% (86% purity)]; (d) Zn, $Br(CH_2)_2Br$, CuBr, LiBr, EtOH, 100 °C (5−6 h), 80°C (16 h for **23** and 3 d for **25**) [70% (99% purity) for (2*Z*,5*Z*)-**23** and 73% (98% purity) for (2*E*,5*Z*)-**25**]; (e) DMP, $Ph_3P{=}CHCO_2Me$, $PhCO_2H$, DMSO, CH_2Cl_2 [71% (85% purity) for **3** and 62% (75% purity) for **5**]; (f) $LiAlH_4$, THF (15%); (g) Zn, $Br(CH_2)_2Br$, EtOH, 100°C (45 min) [50% (96.5% purity)].

Scheme 4. Synthesis of **1** to provide (±)-**1** and (*S*,*E*)-**1**. [The depicted formulas show the synthesis of (*S*,*E*)-**1**]. Reagents: (a) DHP, TsOH, Et_2O [quant. for both (±)- and (*R*)-**32**]: (b) *n*-BuLi, $ClCO_2Me$, THF [91% for (±)-**33**; 77% for (*R*)-**33**]; (c) $LiAlH_4$, Et_2O [44% for (±)-**29**; 48% for (*S*)-**29**]; (d) DMP, wet CH_2Cl_2 [71% for both (±)- and (*S*)-**34**]; (e) $Ph_3P{=}CHCO_2Me$, CH_2Cl_2 [39-44% for (±)-**1**, 71% for (*S*)-**1** of about 17% optical purity]; (d and e in tandem and one-pot manner[21]) DMP, $Ph_3P{=}CHCO_2Me$, $PhCO_2H$, DMSO, CH_2Cl_2 [27% for (±)-**1** and 54% for (*S*)-**1** of about 30% optical purity].

Pheromone synthesis. Part 257: Synthesis of methyl (3*E*,4*Z*,7*Z*)-2,4,7-decatrienoate and methyl (*E*)-2,4,5-tetradecatrienoate, the pheromone components of the male dried bean beetle, *Acanthoscelides obtectus* (Say)

Kenji Mori

Supplementary Data

Experimental part related to Schemes 1 and 2

S1. Methyl (*E*)-2-decen-4-ynoate (8)

A solution of **6** (1.00 g, 10.4 mmol) in Et_3N (3 mL) was added to a stirred mixture of $PdCl_2(Ph_3P)_2$ (100 mg, 0.14 mmol) and **7** (2.10 g, 10 mmol) in dry THF (25 mL). CuI (30 mg, 0.16 mmol) was added to the mixture which was stirred for 4 h at room temperature under argon. The color of the mixture turned from yellow to red, and Et_3NHCl precipitated. The mixture was filtered through Celite, and the Celite layer was washed with Et_2O. The combined filtrate and washings were concentrated in vacuo, and the residue was chromatographed over SiO_2 (20 g). Elution with hexane/EtOAc (50 : 1) gave 1.57 g (84%) of **8**, which was distilled to give 934 mg (50%) of pure **8** as an oil, bp 85°C/2 Torr; n_D^{19}=1.4914; νmax (film): 2954 (s), 2933 (s), 2861 (m), 2215 (m), 1726 (s), 1621 (s), 1459 (m), 1435 (m), 1305 (s), 1266 (s), 1219 (m), 1194 (m), 1176 (m), 1158 (s), 962 (m); δ_H ($CDCl_3$): 0.91 (3H, t, *J* 7.2), 1.30-1.43 (2H, m), 1.56 (2H, m), 2.37 (2H, dt, *J* 2.4, 7.2); 3.75 (3H, s), 6.15 (1H, d, *J* 15.6), 6.76 (1H, dt, *J* 2.4, 15.6); GC-MS [column:HP-5MS, 5% phenylmethylsiloxane, 30 m x 0.25 mm i.d., carrier gas; He; press; 60.7 kPa; temp: 70-230°C (+10°C/min)]: t_R 11.22 min (98.6%); MS (70 eV, EI): *m*/*z*: 180 (2) [M^+], 179 (3), 165 (76), 149 (60), 137 (46), 133 (44), 121 (61), 120 (47), 119 (63), 109 (65), 105 (91), 93 (65), 92 (56), 91 (93), 79 (100), 65 (45), 63 (45), 55 (38), 41 (33). HRMS calcd for $C_{11}H_{16}O_2$: 180.1150, found: 180.1153.

S2. Methyl (*E*)-2-decenoate (9)

5% $Pd/BaSO_4$ (267 mg) was added to a solution of **8** (900 mg, 5 mmol) and quinoline (0.3 mL) in MeOH (15 mL). The mixture was stirred vigorously under H_2 (balloon) for 2 h at room temperature. Then the mixture was filtered through Celite,

and the Celite layer was washed with Et_2O. The filtrate was concentrated in vacuo, and the residue was dissolved in Et_2O. The Et_2O solution was washed successively with dil HCl, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled to give 415 mg (45%) of **9** as a colorless oil, bp 85°C/2 Torr; n_D^{20}=1.4472; νmax (film): 2954 (m), 2928 (s), 2856 (m), 1728 (s), 1658 (m), 1459 (m), 1436 (m), 1271(s), 1197 (s), 1170 (s), 1128 (m), 1041 (m), 980 (m); δ_H ($CDCl_3$): 0.88 (3H, t, *J* 6.8), 1.29 (8H, br. s), 1.45 (2H, t-like, *J* 7.2), 2.19 (2H, q-like, *J* 6.8), 3.73 (3H, s), 5.82 (1H, d, *J* 15.6), 6.97 (1H, dt, *J* 15.6, 6.8); GC-MS (same conditions as those for **8**): t_R 9.76 min (5.6%); 9.96 (9.7%), 10.62 (81.6%, **9**); MS of **9** (70 eV, EI): *m*/*z*: 184 (1) [M^+], 153 (31), 152 (20), 141 (6), 123 (15), 113 (29), 110 (29), 101 (19), 100 (20), 96 (23), 87 (100), 84 (30), 81 (31), 74 (32), 69 (38), 55 (57), 43 (44), 41 (42). HRMS calcd for $C_{11}H_{20}O_2$: 184.1463, found: 184.1462.

S3. 1-Iodo-1,4-heptadiyne (12)

Iodine (15.2 g, 60 mmol) was dissolved in stirred and warmed benzene (170 mL) at 40°C. A solution of morpholine (15.7 g, 180 mmol) in benzene (20 mL) was added dropwise to the above iodine solution with stirring to generate dark orange-colored iodine-morpholine complex. After 10 min, a solution of **10** (5.0 g, 54.3 mmol) in benzene (10 mL) was added to the stirred mixture, and the stirring was continued for 22 h at 45°C (bath temperature). After cooling, the precipitated morpholine hydroiodide was removed by filtration through a glass filter under suction. The filter-cake was washed with Et_2O (25 mL x 3). The combined filtrate and washings were washed successively with $Na_2S_2O_3$ solution, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo to give an oil (16.7 g). This was distilled to give 3.23 g (27%) of **12** as a yellowish oil (The rest polymerized.), bp 72-73°C/4 Torr; n_D^{25}=1.5080; νmax (film): 3295 (w), 2214 (w), 1318 (s), 1308 (s), 1134 (s); δ_H ($CDCl_3$): 1.12 (3H, t, *J* 7.6), 2.14-2.21 (2H, m), 3.32 (2H, t, *J* 2.4); GC-MS (same conditions as those for **8**): t_R 8.33 min (81.3%, **12**), 8.89 (14.3%, probably 1-iodo-1,2-heptadien-4-yne); MS of **12** (70 eV, EI): *m*/*z* : 218 (100) [M^+], 91 (58), 65 (58). HRMS calcd for C_7H_7I: 217.9592, found: 217.9588. Heck reaction of **12** with **13** gave black tar.

S4. 3,6-Nonadiyn-1-ol

This was prepared from 1-bromo-2-pentyne and 3-butyn-1-ol THP ether as reported by Kajiwara et al.[12] as an oil, bp 101-102°C/3 Torr; νmax (film): 3366 (s), 2976 (s),

2938 (s), 2919 (s), 2882 (s), 2213 (w), 1321 (s), 1045 (s); δ_H ($CDCl_3$): 1.12 (3H, t, *J* 7.2), 2.14-2.21 (3H, m), 2.42-2.47 (2H, m), 3.12-3.15 (2H, m), 3.70 (3H, dt *J* 5.2, 6.0); GC-MS (same conditions as those for **8**): t_R 9.12 min (98.3%); MS (70 eV, EI): *m*/*z*: 136 (1) [M^+], 135 (5), 121 (18), 117 (11), 107 (20), 105 (28), 103 (21), 91 (100), 77 (62), 65 (23), 51 (18), 39 (15), 31(10).

S5. (3*Z*,6*Z*)-3,6-Nonadien-1-ol (14)

5% $Pd/BaSO_4$ (1.0 g) was added to a solution of 3,6-nonadiyn-1-ol (1.70 g, 12.5 mmol) and quinoline (0.7 mL) in MeOH (50 mL). The mixture was stirred vigorously under H_2 (balloon) at room temperature for 45 min until the exothermic H_2 uptake ceased. It was then filtered through Celite, and the Celite layer was washed with Et_2O. The filtrate was concentrated in vacuo. The residue was dissolved in Et_2O. The Et_2O solution was washed with dil HCl, $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled to give 1.42 g (81%) of **14** as a colorless oil, bp 80-82°C/3 Torr; νmax (film): 3335 (m), 3011 (m), 2962 (s), 2932 (s), 2874 (m), 1655 (w), 1456 (m), 1049 (s), 968 (m), 720 (m); δ_H ($CDCl_3$): 0.98 (3H, t, *J* 7.2), 1.92-2.14 (3H, m), 2.36 (2H, q *J* 7.2), 2.82 (2H, t, *J* 6.8), 3.65 (2H, t, *J* 6.8), 5.26-5.35 (1H, m), 5.35-5.50 (2H, m), 5.50-5.60 (1H, m); GC-MS (same conditions as those for **8**): t_R 7.54 min (4.6%, nonen-1-ol isomer), 7.61 (80.8%, **14**), 7.70 (7.2%, nonen-1-ol isomer), 7.77 (6.2%, nonen-1-ol isomer); MS of **14** (70 eV, EI): *m*/*z*: 140 (<1) [M^+], 122 (8), 107 (21), 93 (79), 91 (38), 81 (30), 79 (71), 77 (32), 67 (100), 55 (40), 41 (39), 39 (28), 31(13).

S6. Methyl (4*Z*,7*Z*)-4,7-decadienoate (15)

*S6.1. Tosylation of **14**.* TsCl (2.1 g, 11 mmol) was added to a stirred and ice-cooled solution of **14** (1.40 g, 10 mmol) and DMAP (10 mg) in dry pyridine (7 mL). After 2 h at 0-5°C, the mixture was worked up to give 2.54 g (87%) of the tosylate of **14** as a colorless oil, νmax (film): 3011 (m), 2962 (s), 2931 (s), 2873 (m), 1655 (w), 1599 (m), 1362 (s), 1189 (s), 966 (s), 909 (s), 816 (s), 664 (s), 555 (s).

S6.2. (4Z,7Z)-4,7-Decadienenitrile. Powdered KCN (2.50 g, 8.5 mmol) was added to a solution of the above tosylate (2.50 g, 8.5 mmol) in dry DMSO (20 mL). The mixture was stirred for 3 d at room temperature under argon. Work-up yielded 1.28 g (quant.) of the nitrile as a colorless oil, νmax (film): 3012 (m), 2963 (s), 2932 (s), 2873

(m), 2246 (m), 1653 (w), 1456 (m), 1427 (m), 970 (m), 719 (m); GC-MS (same conditions as those for **8**): t_R 9.11 min (0.9%, decenenitrile isomer), 9.22 (5.5%, decenenitrile isomer), 9.27 (4.7%, decenenitrile isomer), 9.34 (76.8%, the desired nitrile), 9.44 (4.6%, decenenitrile isomer), 9.49 (3.3%, isomer of the desired nitrile); MS of the desired nitrile (70 eV, EI): *m*/*z*: 149 (6) [M^+], 148 (14), 134 (14), 120 (63), 108 (14), 93 (27), 79 (94), 67 (100), 55 (51), 41 (38).

S6.3. (4Z,7Z)-4,7-Decadienoic acid. A solution of the above nitrile (1.25 g, 8.4 mmol) and NaOH (4.0 g, 100 mmol) in 99% EtOH (20 mL) and water (6 mL) was stirred and heated under reflux for 6 h. Usual work-up gave 1.23 g (87%) of the acid as a colorless oil, νmax (film): ~3500- ~2500 (br, m), 3012 (s), 2963 (s), 1713 (s), 1413 (m), 1283 (m), 967 (m), 948 (m), 727 (m).

*S6.4. Methyl (4Z,7Z)-4,7-decadienoate (**15**).* A solution of the above acid (1.20 g, 7 mmol) in Et_2O (10 mL) was treated with CH_2N_2 (prepared from 2.5 g of *N*-methyl-*N*-nitrosourea) in Et_2O (70 mL), and concentrated in vacuo. The residue was distilled to give 962 mg (80%) of **15** as a colorless oil, bp 82-85°C/3 Torr; νmax (film): 3011 (m), 2961 (m), 2933 (m), 2873 (m), 1742 (s), 1654 (w), 1437 (m), 1199 (m), 1164 (m), 969 (w), 728 (w). Its ^{1}H NMR spectrum was complicated due to the extensive double bond isomerization and migration in the course of the nitrile hydrolysis. GC-MS (same conditions as those for **8**): t_R 9.73 min (1%, decenoate isomer), 9.81 (44%,**15**), 9.84 [20%, (4*E*,7*Z*)-isomer of **15**], 9.89 (8%, (4*Z*,7*E*)-isomer of **15**], 9.93 [4%, decenoate isomer), 9.99 [3%, (4*E*,7*E*)-isomer of **15**], 10.40 [(6%, (5*Z*,7*Z*)-conjugated isomer], 10.47 [11%, (5*E*,7*Z*)-conjugated isomer], 10.57 [0.5%, (5*Z*,7*E*)-conjugated isomer], 10.63 [0.5%, (5*E*,7*E*)-conjugated isomer]. Accordingly, the composition of the product was 44% of (4*Z*,7*Z*)-**15**, 31% of other *E*/*Z*-isomers of **15**, 18% of the conjugated diene isomers with strong M^+ at *m*/*z* 180, and 5% of decenoate isomers. Assignments of *E*/*Z* geometries of the components are tentative and speculative.

S7. Methyl (2*RS*,4*Z*,7*Z*)-2-phenylselenenyl-4,7-decadienoate (16)

A solution of $KN(SiMe_3)_2$ (TCI, 0.5 M in toluene, 30 mL, 30 mmol) was added dropwise to a stirred and cooled solution of crude **15** (887 mg, 4.9 mmol) in THF (20 mL) at -78 to -65°C under argon. The stirring was continued for 30 min at -78°C to generate a pale orange-colored enolate solution. Then a red solution of PhSeCl (1.53 g,

8 mmol) in THF (20 mL) was added dropwise at -78 to -65°C, and the mixture was stirred for 30 min at -78 to -70°C. The reaction was quenched by the addition of NH_4Cl solution, and the mixture was extracted with Et_2O. The Et_2O solution was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed over SiO_2 (30 g). Elution with hexane/EtOAc (200 : 1) gave Ph_2Se_2 (70 mg), and further elution with the same eluent gave 878 mg (48%) of **16** as a yellowish viscous oil, νmax (film): 3058 (w), 3010 (m), 2959 (s), 2930 (s), 2872 (m), 1732 (s), 1653 (w), 1578 (m), 1437 (m), 1250 (m), 1160 (m), 741 (s), 691 (s); δ_H ($CDCl_3$) (Major signals due to **16** are recorded.): 0.96 (3H, t, *J* 7.2), 1.90-2.10 (4H, m), 2.45-2.60 (1H, m), 2.60-2.80 (2H, m), 3.63 (3H, s), 5.10-5.55 (4H, m), 7.20-7.45 (3H, m), 7.55-7.65 (1H, m), 7.65-7.70 (1H, d-like , *J* 6.8); GC-MS (same conditions as those for **8**): t_R 19.26 min (58.3%, **16**), 19.51 [7.6%, (4*E*,7*Z*)-isomer of **16**]; Other isomers of **16** with $(M+1)^+$=338 : 19.88 (4.5%), 20.17 (3.7%); Dihydro isomers of **16** with $(M+1)^+$= 340 : 19.20 (5.1%), 19.32 (7.9%), 19.40 (2.8%). MS of **16** (70 eV, EI): *m*/*z*: 338 (21) [$(M+1)^+$], 243 (11), 181 (17), 169 (18), 157 (51), 149 (42), 138 (16), 121 (100), 120 (44), 93 (38), 91 (39), 79 (63), 77 (46), 67 (31), 55 (38), 41 (29).

S8. Methyl (2*E*,4*E*,7*Z*)-2,4,7-decatrienoate (5)

A solution of **16** (474 mg, 1.4 mmol) in THF (16 mL) was added dropwise to a stirred suspension of $NaIO_4$ (2.14 g, 10 mmol) in water (10 mL) at room temperature. The reaction was slightly exothermic. The mixture was stirred for 1 h at room temperature, diluted with Na_2CO_3 solution, and extracted with Et_2O. The Et_2O solution was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed over SiO_2 (20 g). Elution with pentane/EtOAc (30 : 1) gave 113 mg of crude **5** as a slightly yellowish oil, νmax (film): 3013 (m), 2960 (s), 2932 (s), 2873 (m), 1721 (s), 1643 (s), 1617 (m), 1435 (m), 1268 (s), 1139 (s), 1001 (m); δ_H ($CDCl_3$) 0.85-0.92 (1.6 H, m, due to decadienoate isomers), 0.96 (3H, t, *J* 7.2), 1.25-1.40 (1.8H, m, due to decadienoate isomers), 2.00-2.10 (2H, m), 2.92 (2H, t, *J* 6.8), 3.74 (3H, s), 5.30-5.42 (1H, m), 5.43-5.56 (1H, m), 5.25-5.40 (1.4H, due to impurities), 6.05-6.24 (2H, m), 7.27 (1H, dd, *J* 10, 16); GC-MS (same conditions as those for **8**): t_R 10.38 (6.2%, decadienoate isomer), 10.43 (1.4%, decadienoate isomer), 10.51 (2.9%, decadienoate isomer), 10.55 (9.8%, decadienoate isomer), 10.87 [3.0%, (2*E*,4Z,7*Z*)-**3** = natural component], 10.93 (2.0%, decadienoate isomer), 10.97 (1.7%, isomer of **3**), 11.17 (1.8%, isomer of **3**), 11.39 [60.8%, (2*E*,4*E*,7*Z*)-**5**], 11.49 (1.5%, isomer of **3**), 11.86 (0.7%, isomer of **3** with a large M^+ peak), 12.14 (1.8%, isomer of **3** with a large

M^+ peak). Use of Na_2CO_3 at the work-up stage might have caused the isomerization of **3** to **5**. MS of **5** (70 eV, EI): *m*/*z*: 180 (13) [M^+], 149 (19), 138 (14), 137 (9), 133 (10), 124 (14), 121 (45), 120 (34), 119 (45), 111 (77), 105 (39), 98 (42), 93 (30), 91 (87), 81 (33), 79 (100), 77 (48), 68 (21), 67 (21), 65 (22), 59 (21), 55 (32), 53 (22), 39 (27).

S9. (*Z*)-3-Hexenal

According to Wavrin and Viala,[14] DMP (10.0 g, 23.6 mmol) was added portionwise to a stirred and ice-cooled solution of **17** (TCI, *Z*/*E* = 99.2 : 0.6 as analyzed by GC-MS, 2.0 g, 20 mmol) in CH_2Cl_2 (20 mL) at 0-5°C under argon. The mixture was stirred for 1 h at room temperature, and quenched by adding a solution of $NaHCO_3$ and $Na_2S_2O_3$. After stirring for 10 min, the mixture was diluted with Et_2O, and filtered through Celite. The Celite layer was washed with Et_2O. The Et_2O layer of the filtrate was separated, washed with brine, dried ($MgSO_4$), and concentrated under atmospheric pressure. The residue was diluted with dry C_6H_6, and concentrated under atmospheric pressure to give a solution of (*Z*)-3-hexenal in C_6H_6 (ca. 10 mL). This was employed in the next step. A small portion of the solution was further concentrated to give crude (*Z*)-3-hexenal, νmax (film): 2724 (w), 1725 (s), 1656 (m): MS (70 eV, EI): *m*/*z*: 98 (12) [M^+], 83 (27), 80 (19), 69 (57), 55 (46), 41 (100), 39 (41).

S10. (±)-(*Z*)-5-Octen-1-yn-3-ol (18)

A solution of MeMgBr in Et_2O (TCI, 3 M, 20 mL, 60 mmol) was added to a stirred and cooled solution of TMSC ≡ CH (6.60 g, 66 mmol) in dry THF (30 mL) at -70°C under argon. The mixture was stirred for 3 h at 30°C until the evolution of CH_4 ceased. Then a C_6H_6 solution (10 mL) of crude (*Z*)-3-hexenal prepared from 2.0 g of **17** was added dropwise to the stirred and cooled solution of TMSC ≡ CMgBr at -78°C, and the mixture was left to stand overnight. It was then poured into ice and NH_4Cl solution, and extracted with Et_2O. The Et_2O solution was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to give crude TMS derivative of **18**, MS (70 eV, EI): *m*/*z* 181 (12) [M^+-1], 127 (59), 99 (100), 75 (31), 73 (21), 70 (19). K_2CO_3 (4.0 g, 29 mmol) was added to a solution of the TMS derivative in MeOH (60 mL) and water (2 mL), and the mixture was stirred for 1 h at 50°C. It was then concentrated in vacuo. The residue was diluted with water, and extracted with Et_2O. The Et_2O solution was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled to give 920 mg (37%, three steps) of **18** as a colorless oil, bp 60-62°C/5

Torr; νmax (film) ~3400 (br. s), 3303 (s), 3013 (m), 2965 (s), 2934 (m), 2875 (m), 2116 (w), 1654 (w), 1041 (s), 656 (s); δ_H ($CDCl_3$): 0.98 (3H, t, *J* 7.6), 1.71 (1H, d, *J* 7.2), 2.10 (2H, dq, *J* 7.2, 7.2), 2.47 (1H, d, *J* 2.0), 2.50 (2H, dd, *J* 6.4, 7.2), 4.40 (1H, dt, *J* 2.0, 6.4), 5.41-5.48 (1H, m), 5.61-5.67 (1H, m); GC-MS (same conditions as those for **8**): t_R 5.02 min (90.3%); MS (70 eV, EI) : *m*/*z*: 124 (2) [M^+], 123 (2), 109 (22), 95 (42), 91 (49), 70 (49), 69 (42), 67 (64), 55 (81), 41 (100), 39 (38).

S11. (±)-Methyl (7*Z*)-3,4,7-decatrienoate (19)

Propanoic acid (0.1 g) was added to a solution of (±)-**18** (0.90 g, 7.3 mmol) in methyl orthoacetate (20 mL), and the mixture was stirred and heated at 145°C (bath temperature) for 1 h with distillative removal of the low bp materials. After cooling, the mixture was concentrated in vacuo. The residue was diluted with methyl orthoacetate (10 mL) and *o*-xylene (10 mL) containing propanoic acid (0.1 g), and heated at 160-170°C (bath temperature) for 1 h. After cooling, the mixture was concentrated in vacuo. The residue was distilled to give 1.11 g (85%) of (±)-**19** as a colorless oil, bp 93-95°C/6 Torr; νmax (film) 3010 (m), 2964 (m), 2875 (m), 1967 (w), 1742 (s), 1653 (w), 1166 (s); δ_H ($CDCl_3$): 0.96 (3H, t, *J* 7.2), 2.08-2.11 (2H, m), 2.73-2.76 (2H, m), 3.04 (2H, dd, *J* 2.4, 7.2), 3.70 (3H, s), 5.17-5.21 (1H, m), 5.24-5.28 (1H, m), 5.33-5.39 (1H, m), 5.41-5.48 (1H, m); GC-MS [same conditions as those for **8**]: t_R 9.58 min (12.7%, unidentified), 10.26 [0.8%, (7*E*)-isomer of **19**], 10.33 (80.8%, **19**). MS of **19** (70 eV, EI): *m*/*z*: 180 (4) [M^+], 165 (3), 151 (9), 137 (7), 123 (23), 121 (32), 120 (22), 106 (50), 105 (42), 93 (54), 91 (100), 79 (66), 77 (38), 69 (28), 67 (29), 55 (24), 41 (62).

S12. Thermal isomerization of (±)-19 over basic alumina

Al_2O_3 (Aldrich 199443, basic Brockmann 1, 3.0 g) was placed in a 30 mL round-bottomed flask, and heated at 200°C (bath temperature) for 2 h under reduced pressure (4 Torr). After cooling, a solution of (±)-**19** (1.02 g, 5.6 mmol) in *o*-xylene (6 mL) was added to Al_2O_3 which turned yellow in color, and the mixture was vigorously stirred and heated at 160°C (bath temperature) for 2 h under argon. After cooling, the mixture was filtered through a glass filter, and Al_2O_3 was washed with EtOAc (10 mL). The combined filtrate and washings were concentrated in vacuo. The residue was distilled to give 0.423 g (41%) of a slightly yellowish oil, bp 100-102°C/5 Torr; νmax (film): 3502 (w, due to **18**), 3299 (w, due to **18**), 3013 (s), 2964 (s), 2934 (s), 2874 (s),

2113 (w, due to **18**), 1967 (w, due to the recovered **19**), 1741 (s, due to **19**), 1720 (s), 1637 (s), 1603 (w), 1436 (m), 1268 (s), 1170 (s), 994 (m). The distillate was a mixture containing 6% of **18**, 21% of **19**, 38% of (2*E*,4*Z*,7*Z*)-**3** and total 25% of isomers of **3** as revealed by GC analysis. GC-MS (same conditions as those for **8**): t_R 4.98 min (6.3%, **18**), 10.31 (20.9%, **19**), 10.88 [37.8%, (2*E*,4*Z*,7*Z*)-**3**], 11.64 (17.8%, an isomer of **3** with strong M^+ at *m*/*z* 180). MS of (2*E*,4*Z*,7*Z*)-**3** (70 eV, EI): *m*/*z*: 180 (4) [M^+], 165 (2), 149 (13), 137 (15), 121 (50), 120 (38), 119 (34), 111 (52), 105 (40), 98 (27), 93 (35), 91 (88), 79 (100), 77 (49), 67 (21), 65 (22), 55 (30), 39 (27). The MS was identical to that of the naturally occurring pheromone component.