

Organoselenium-Assisted Route to Conjugated Dienoic Macrolides. Synthesis of (*Z*)-Dodec-3-en-12-olide, a Pheromone of the Flat Grain Beetle *Cryptolestes pusillus* (Coleoptera: Cucujidae)

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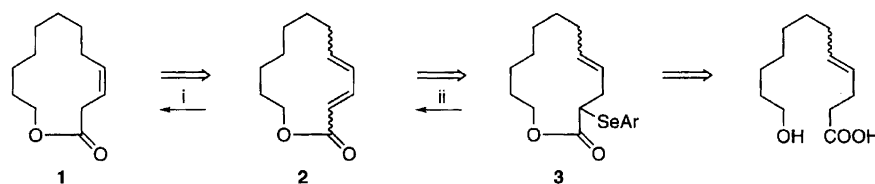
Oxidative elimination of the arylseleno group in (*E*)-2-(4-methoxyphenylseleno)dodec-4-en-12-olide gave (*Z,Z,E*)-dodeca-2,4-diene-12-olide which on 1,4-*cis*-hydrogenation over (η^6 -naphthalene)tricarbonylchromium afforded the title pheromone. (*E*)-2-(4-Methoxyphenylseleno)dodec-4-en-12-olide was best prepared by macrolactonization of the corresponding ω -hydroxy acid.

Access to (*Z*)-olefinic macrolides (e.g., the pheromones of cucujid beetles) remained limited until PPh_3 -DEAD was introduced as a reagent for macrolactonization,^{1,2} and was applied to pheromone synthesis by Boden *et al.*³ Whether chemical^{3,4a-j} or enzymatic,^{4k-m} most synthetic schemes leading to (*Z*)-olefinic macrolides have involved a lactonization of the corresponding hydroxy acid in the final step. Having developed effective syntheses of (*Z*)-olefinic insect pheromones by 1,4-*cis*-hydrogenation of conjugated dienes over (η^6 -arene)tricarbonylchromium catalysts,^{5,6} we thought it would be interesting to examine a similar approach to (*Z*)-olefinic macrolides such as compound **1** (Scheme 1). The required 2,4-dienolides **2**, we reasoned, could be obtained by oxidative elimination of an ArSe group⁷ from the corresponding α -arylseleno olefinic macrolide **3**. Similar transformations have recently been carried out in acyclic systems using an improved procedure⁸ for α -selenation of esters. Thus, the protocol for preparing *cis*-olefinic macrolides (Scheme 1)

would require ω -hydroxy- γ -alkenoic acids as starting materials.

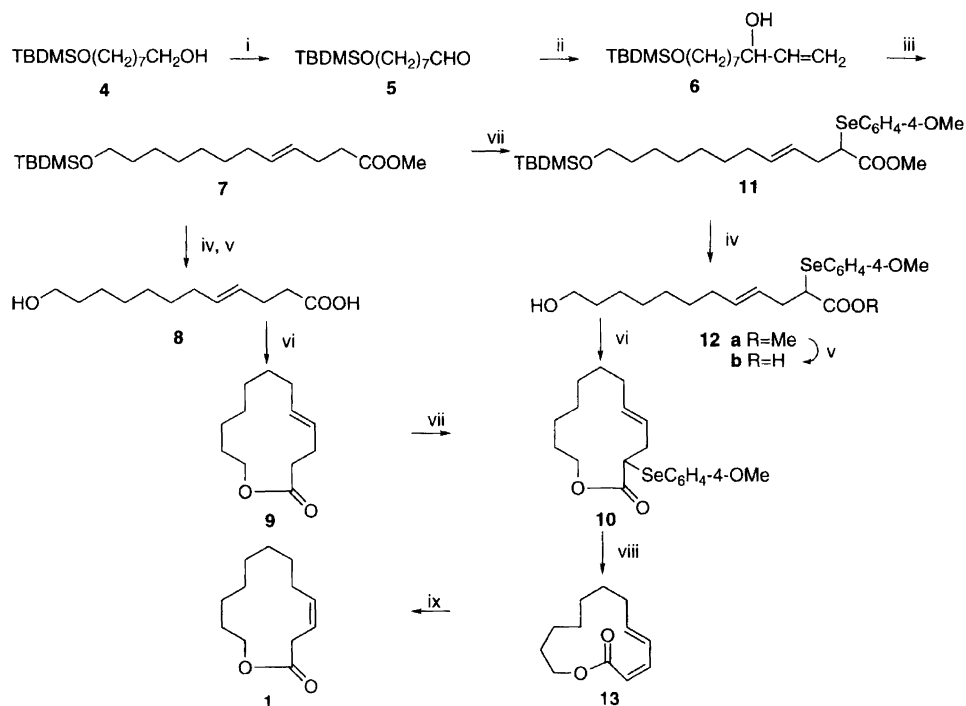
Results and discussion

Readily available 8-hydroxyoctyl *tert*-butyldimethylsilyl ether (**4**)⁹ was used as the starting material in the synthesis of compound **1**, the major component of the aggregation pheromone of the flat grain beetle *Cryptolestes pusillus* (Coleoptera: Cucujidae)¹⁰ (Scheme 2). The remaining primary alcohol was then electrochemically oxidized in a TEMPO mediated reaction¹¹ to give aldehyde **5** (88%). Although PCC oxidation also affords the desired aldehyde in high yield,⁹ the electrochemical approach is environmentally more attractive. Subsequent addition of vinylmagnesium bromide, treatment of the resulting alcohol **6** with trimethyl orthoacetate and *E*-stereoselective Claisen–Johnson rearrangement¹² afforded the key intermediate **7** in 61% overall yield.



Scheme 1. i, H_2 -(arene) $\text{Cr}(\text{CO})_3$; ii, H_2O_2 -THF.

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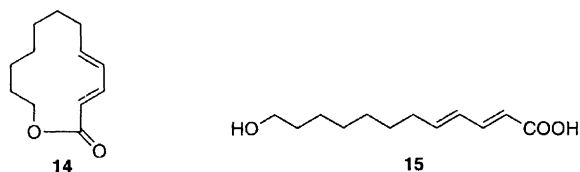
Scheme 2. i, NaBr–NaHCO₃aq–CH₂Cl₂–4–AcNH–TEMPO (–2e[–], 2.0 F mol^{–1}), rt; ii, H₂C=CHMgBr–THF; iii, MeC(OMe)₃–EtCO₂H (cat.), 115 °C; iv Bu₄NF–THF; rt; v, (a) KOH–H₂O–MeOH, rt; (b) HCl aq; vi, Ph₃P–DEAD–MePh; vii, (a) LDA–THF, –78 °C (b) (4–MeOC₆H₄)₂Se₂; viii, H₂O₂–THF, rt; ix, H₂–(η⁶-naphthalene)Cr(CO)₃–THF, 45 °C, 40 atm.

Compound **7** was further transformed in two ways, differing in the order of the α -arylselenation and macrocyclization steps. Removal of the silyl protective group and saponification of the ester afforded the unsaturated acid **8** in 68% yield. Subsequent lactonization proceeded without affecting the double bond geometry to give (*E*)-dodeca-4-en-12-olide (**9**) in moderate yield (31%). Final α -(4-methoxyphenyl)selenation of compound **9** afforded the selenated lactone **10** in 73% yield (15% based on **7**).

α -(4-Methoxyphenyl)selenation of compound **7** afforded the *O*-silylated unsaturated ester **11** in 65% yield. Removal of the silyl protective group (74% yield) and saponification of the ester (81% yield) gave the unsaturated acid **12b**. Lactonization under Mitsunobu conditions afforded the α -selenated lactone **10** in 63% yield (25% based on **7**). Thus, the latter route is clearly the more efficient one.

Oxidative elimination of the arylseleno moiety in compound **10** proceeded cleanly (91% yield) to afford (2*Z*,4*E*)-dodeca-2,4-dien-12-olide (**13**). The configurational assignment is based on decoupling experiments [δ 5.56 (d, $J_{2,3}$ = 11.1 Hz, 2-H), 6.64 (dd, $J_{2,3}$ = $J_{3,4}$ = 11.1 Hz, 3-H), 7.30 (dd, $J_{4,5}$ = 16.0, $J_{3,4}$ = 11.1 Hz, 4-H), 6.11 (t, $J_{4,5}$ = 16.0, $J_{5,6}$ = 4.3 Hz, 5-H)]. These values are in good agreement with those reported for acyclic (2*Z*,4*E*)-methyl deca-2,4-dienoate.¹³ The transition state for *syn*-elimination to a (2*Z*)-double bond is apparently conformationally less strained than the one affording the (2*E*)-isomer. (η^6 -Naphthalene)tricarboxylchromium is usually the catalyst of choice for 1,4-*cis*-hydrogenation of 1,3-dienes. Whereas other (η^6 -arene)tricarboxylchromium

catalysts require higher temperatures (for a review, see Ref. 14), the naphthalene derivative is effective at temperatures as low as 45 °C. In the small-scale autoclave hydrogenation of compound **13** tried (40 mg dissolved in 10 ml of THF), a 4.5 molar excess of the catalyst was used in order to accelerate the reaction and to minimize the risk of catalyst destruction by traces of oxygen. With these precautions, target pheromone **1** was isolated in 65% yield after hydrogenation. Supposedly, the *Z,E*-diene moiety of compound **13** is readily coordinated to zero-valent chromium. However, by analogy with 1,4-*cis*-hydrogenation of acyclic dienes, one could expect the (2*E*,4*E*)-dodeca-2,4-dien-12-olide (**14**) to be an even more reactive precursor of lactone **1**. In order to examine this route to the product in some detail, compound **11** was subjected to desilylation, oxidative elimination and saponification to yield (2*E*,4*E*)-12-hydroxydodeca-2,4-dienoic acid (**15**). However, all attempts to lactonize this material using PPh₃–DEAD met with failure. This reluctance of the (2*E*,4*E*)-dienoic acid to undergo lactonization highlights the advantage of our α -arylselenation–macrolactonization–oxidative elimination route to conjugated dienoic macrolides, and, following 1,4-*cis*-hydrogenation,



Scheme 3.

to (*Z*)-alk-3-ene- ω - or (*Z*)-alk-3-ene-($\omega-1$)-olide semiochemicals of cucujid grain beetles. The unoptimized overall yield of pheromone **1** from silyl ether **4** was 10.5% over the nine steps used.

Experimental

All melting points are uncorrected. NMR spectra were recorded for samples in CDCl₃ at 299.903 MHz (¹H) and at 75.419 MHz (¹³C) using a Varian XL-300 spectrometer. Multiplicities of signals in the ¹H NMR spectra are given as observed. Elemental analyses were performed by Analytical Laboratories, Lindlar, Germany. Bis(4-methoxyphenyl) diselenide¹⁵ and (η^6 -naphthalene)Cr(CO)₃ (Ref. 16) were prepared according to the literature. THF, *i*-Pr₂NH, pyridine, toluene and CH₂Cl₂ were purified by conventional procedures and redistilled prior to use. 1,8-Octanediol, *tert*-butyldimethylchlorosilane, trimethyl orthoacetate, diethyl azodicarboxylate (DEAD) and triphenylphosphine were used as purchased. 8-(*tert*-Butyldimethylsilyloxy)-1-octanol (**4**) was prepared in 59% yield, essentially (pyridine was used as solvent instead of dichloromethane) as described.⁹

8-(*tert*-Butyl) dimethylsilyloxyoctanal (**5**). An undivided glass cell, equipped with a magnetic stirring bar and an outer cooling jacket, was charged with compound **4** (1.54 g, 6 mmol), 4-acetamido-2,2,6,6-tetramethyl piperidin-1-oxyl (4-AcNH-TEMPO) (0.3 g) in CH₂Cl₂ (15 ml), and a solution of NaBr (25%) and NaHCO₃ (5%) in water (20 ml). The cathode (stainless steel, 17 × 25 mm) and anode (graphite plate, 13 × 25 mm) were immersed, at a distance of 10 mm, into the upper aqueous layer of the biphasic system. The mixture was then electrolysed under a constant current of 150 mA at ambient temperature with moderate magnetic stirring of the lower phase. The electrolysis was continued until the consumption of starting material was practically complete (TLC monitoring). This required 2.0 F mol⁻¹, based on alcohol **4**, and was accompanied by a colour change in the organic phase. The lower organic layer was separated, filtered, dried (MgSO₄), and concentrated to leave essentially pure aldehyde **5** as a yellowish oil (1.355 g, 88%). This was immediately used in the next step without further purification. ¹H NMR spectral data of the material were in good agreement with literature data.⁹

Methyl (*E*)-12-(*tert*-butyl) dimethylsilyloxydodec-4-enoate (**7**). To a stirred solution of vinylmagnesium bromide (30 mmol) in THF (15 ml), a solution of aldehyde **5** (4.71 g, 18.5 mmol) in THF (10 ml) was added dropwise at 30 °C. After 2 h of additional stirring, the reaction mixture was quenched with an aqueous solution of NH₄Cl and extracted with Et₂O. The extracts were dried (MgSO₄) and concentrated under vacuum. The residue was co-evaporated with toluene, and the resulting crude vinyl carbinol **6** was used in the following step without purification. The material was heated with MeC(OMe)₂

(25 ml) and propionic acid (0.2 ml) for 5 h until no more methanol distilled off. The reaction mixture was then concentrated under reduced pressure and the remainder was stirred with HOAc-acidified brine for 5 min and then neutralized with solid NaHCO₃. After extraction with benzene, drying over MgSO₄ and evaporation of the solvent, column chromatography (elution with pentane–EtOAc 9:1) afforded the title compound as a colourless oil. Yield: 3.9 g (61%). ¹H NMR: δ 0.03 (s, 6 H), 0.88 (s, 9 H), 1.28 (m, 8 H), 1.49 (m, 2 H), 1.95 (m, 2 H), 2.30–2.35 (m, 4 H), 3.58 (t, 2 H, *J* = 6.6 Hz), 3.65 (s, 3 H), 5.41 (m, 2 H). ¹³C NMR: δ –5.3 (q), 18.4 (s), 25.7 (t), 26.0 (q), 27.9 (t), 29.1 (t), 29.3 (t), 29.4 (t), 32.5 (t), 32.8 (t), 34.2 (t), 51.4 (q), 63.3 (t), 127.8 (d), 131.8 (d), 173.7 (s). Analysis: calc. for C₁₉H₃₈O₃Si: C, 66.61; H, 11.18. Found: C, 66.40; H, 11.70.

(*E*)-12-Hydroxydodec-4-enoic acid (**8**). To a solution of ester **7** (0.855 g, 2.5 mmol) in THF (25 ml) tetrabutylammonium fluoride (2.65 mmol, 2.65 ml of a 1 M solution in THF) was added, and the mixture was stirred for 5 h at ambient temperature. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (using a gradient of pentane and 10 → 40% EtOAc as the eluent) to afford crude (*E*)-methyl 12-hydroxydodec-4-enoate. The ester was dissolved in MeOH (6 ml) and treated with KOH (0.4 g) in water (2 ml) at ambient temperature over 1 h. Methanol was removed *in vacuo*, the residue was diluted with brine (5 ml) and unconverted material was taken up in Et₂O. The aqueous layer was acidified with 2 M HCl and extracted with Et₂O. The extract was washed with brine, dried (Na₂SO₄) and evaporated to afford the title compound (0.366 g, 68%) as white crystals, m.p. 60–61 °C. ¹H NMR: δ 1.30 (m, 8 H), 1.56 (m, 2 H), 1.98 (q, 2 H, *J*_{5,6} = *J*_{6,7} = 6.6 Hz), 2.33 (m, 2 H), 2.41 (m, 2 H), 3.64 (t, 2 H, *J* = 6.6 Hz), 5.30 (br s, 2 H), 5.43 (m, 2 H). Analysis: calc. for C₁₂H₂₂O₃: C, 67.26; H, 10.35. Found: C, 67.44; H, 10.51.

(*E*)-Dodec-4-en-12-olide (**9**). A solution of acid **8** (0.354 g, 1.65 mmol) in a mixture of THF (10 ml) and toluene (45 ml) was added over 7 h to a stirred solution of Ph₃P (2.157 g, 8.27 mmol) and DEAD (1.451 g, 1.31 ml, 8.41 mmol) in toluene (257 ml) under N₂ with a syringe pump. The solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography (using a gradient of pentane and 0 → 5% Et₂O as the eluent) to give 0.099 g (31%) of the title compound as a colourless oil. ¹H NMR: δ 1.28 (m, 4 H), 1.40 (m, 4 H), 1.64 (m, 2 H), 2.01 (q, 2 H, *J*_{5,6} = *J*_{6,7} = 5.5 Hz), 2.38 (m, 4 H), 4.12 (m, 2 H), 5.41 (dt, 1 H, *J* = 15.5 and 6.2 Hz), 5.52 (dt, 1 H, *J* = 15.5 and 6.2 Hz). ¹³C NMR: δ 24.7 (t), 26.5 (t), 27.0 (t), 27.1 (t), 28.1 (t), 31.6 (t), 34.6 (t), 64.5 (t), 128.5 (d), 132.7 (d), 173.9 (s).

(E)-2-(4-Methoxyphenylseleno)dodec-4-en-12-olide (**10**):

Procedure A. To a stirred solution of *i*-Pr₂NH (0.091 g, 0.9 mmol) in THF (1.1 ml) at -78°C , a solution of *n*-BuLi in hexane (0.46 ml 1.55 M, 0.72 mmol) was added dropwise. After 10 min, a solution of macrolide **9** (0.071 g, 0.36 mmol) in THF (0.4 ml) was added over 5 min, and the mixture was stirred for an additional 30 min. The solution of the lithium enolate thus formed was then transferred via cannula at -78°C into a stirred solution of bis-(4-methoxyphenyl) diselenide (0.18 g, 0.48 mmol) in THF (1.1 ml), and stirring was continued for another 40 min. The reaction mixture was quenched with HOAc (0.2 ml) and neutralized with aqueous NaHCO₃. After extraction with Et₂O, drying (Na₂SO₄) and concentration, column chromatography (using pentane containing 2→5% Et₂O as the eluent) afforded 0.102 g (73%) of lactone **10** as a viscous oil. ¹H NMR: δ 1.2–1.44 (m, 8 H), 1.5–1.75 (m, 2 H), 1.97 (m, 2 H), 3.61 (dd, 1 H, *J*=11.1 and 4.8 Hz), 3.80 (s, 3 H), 3.82 (ddd, 1 H, *J*=11.1, 7.7 and 3.1 Hz), 4.40 (ddd, 1 H, *J*=11.1, 7.3 and 3.1 Hz), 5.38 (dm, 2 H, *J*_{4,5}=15.7 Hz), 5.52 (dt, 1 H, *J*_{4,5}=15.7, *J*_{5,6}=7.0 Hz), 6.83 (d, 2 H, *J*=8.6 Hz), 7.54 (d, 2 H, *J*=8.6 Hz). ¹³C NMR: δ 24.5 (t), 26.6 (t), 26.7 (t), 27.0 (t), 27.1 (t), 31.8 (t), 35.2 (t), 43.2 (d), 55.2 (q), 65.0 (t), 114.6 (d), 117.8 (s), 126.9 (d), 134.5 (d), 138.0 (d), 160.2 (s), 173.0 (s). Analysis: calc. for C₁₉H₂₆O₃Se: C, 59.84; H, 6.87. Found: C, 59.78; H, 6.73.

Procedure B. A solution of acid **12b** (0.196 g, 0.49 mmol) in toluene (17 ml) was introduced by syringe pump over 6 h into a stirred solution of Ph₃P (0.64 g, 2.45 mmol) and DEAD (0.435 g, 0.394 ml, 2.50 mmol) in toluene (77 ml) at ambient temperature under an atmosphere of N₂. The mixture was concentrated *in vacuo*, after which column chromatography (using pentane containing 0→5% Et₂O as the eluent) afforded 0.119 g (63%) of lactone **10**, identical with the material obtained by using procedure A.

Methyl (E)-12-(tert-butyl)dimethylsilyloxy-2-(4-methoxyphenylseleno)dodec-4-enoate (11). To a stirred solution of *i*-Pr₂NH (0.758 g, 7.5 mmol) in THF (9 ml), *n*-BuLi in hexane (3.87 ml 1.55 M, 6 mmol) was added dropwise at -78°C . After 10 min, a solution of ester **7** (1.028 g, 3 mmol) in THF (3 ml) was added over 5 min, and the mixture was stirred for an additional 30 min. The lithium enolate solution thus formed was transferred via cannula at -78°C into a stirred solution of bis(4-methoxyphenyl) diselenide (1.49 g, 4.02 mmol) in THF (9 ml), and stirring was continued for another 40 min. The reaction mixture was quenched with HOAc (1 ml) and neutralized with NaHCO₃ (5% aq.). The products were extracted into Et₂O and the combined extracts were dried (MgSO₄) and concentrated. Column chromatography (using a gradient of pentane and 2→10% Et₂O) gave the title compound (1.03 g, 65%) as a viscous oil. ¹H NMR: δ 0.04 (s, 6 H), 0.88 (s, 9 H), 1.27 (m, 8 H), 1.49 (m, 2 H), 1.95 (m, 2 H), 2.39 (m, 1 H), 2.51 (m,

1 H), 3.52 (dd, 1 H, *J*=9.3 and 6.7 Hz), 3.53 (t, 2 H, *J*=6.6 Hz), 3.61 (s, 3 H), 3.80 (s, 3 H), 5.33 (dt, 1 H, *J*=15.1 and 6.2 Hz), 5.48 (dt, 1 H, *J*=15.1 and 7.2 Hz), 6.83 (d, 2 H, *J*=8.8 Hz), 7.50 (d, 2 H, *J*=8.8 Hz). ¹³C NMR: δ -5.3 (q), 18.3 (s), 25.7 (t), 26.0 (q), 29.0 (t), 29.2 (t), 32.5 (t), 34.8 (t), 43.1 (d), 51.9 (q), 55.2 (q), 63.3 (t), 114.6 (d), 117.5 (s), 125.9 (d), 134.0 (d), 138.2 (d), 160.3 (s), 173.0 (s). Analysis: calc. for C₂₆H₄₄O₄SeSi: C, 59.18; H, 8.41. Found: C, 59.46; H, 8.92.

Methyl (E)-12-hydroxy-2-(4-methoxyphenylseleno)dodec-4-enoate (12a). A solution of ester **11** (0.819 g, 1.55 mmol) in THF (15 ml) was treated with tetrabutylammonium fluoride (1.7 mmol, 1.7 ml of an 1 M solution in THF) at ambient temperature for 4 h. Removal of the solvent under reduced pressure and subsequent column chromatography (10%, then 30% EtOAc in pentane) afforded 0.475 g (74%) of the title compound as a viscous oil. ¹H NMR: δ 1.28 (m, 9 H), 1.54 (m, 2 H), 1.95 (q, *J*_{5,6}=*J*_{6,7}=7.0 Hz, 2 H), 2.41 (m, 2 H), 2.51 (m, 1 H), 3.52 (dd, *J*=9.3, 6.8 Hz, 1 H), 3.61 (s, 3 H), 3.67 (t, 2 H), 3.80 (s, 3 H), 5.33 (dt, *J*=15.5, 6.6 Hz, 1 H), 5.47 (dt, *J*=15.5, 6.6 Hz, 1 H). ¹³C NMR: δ 25.6 (t), 28.9 (t), 29.1 (t), 29.2 (t), 32.4 (t), 32.7 (t), 34.8 (t), 43.1 (d), 51.9 (q), 55.2 (q), 63.0 (t), 114.6 (d), 117.5 (s), 126.0 (d), 133.9 (d), 138.2 (d), 160.3 (s), 173.0 (s).

(E)-12-Hydroxy-2-(4-methoxyphenylseleno)dodec-4-enoic acid (12b). A solution of ester **12a** (0.25 g, 0.6 mmol) in MeOH (2 ml) was stirred to homogeneity at ambient temperature with a 20% aqueous solution of KOH (1 ml) over 5 h. The solution was then diluted with saturated sodium chloride solution (brine) and extracted with Et₂O to remove unsaponified material. The aqueous phase was acidified with 2 M HCl and extracted with Et₂O. The extracts were washed with brine, dried (Na₂SO₄), and concentrated to give 0.196 g (81%) of the title compound as a viscous, colourless oil. ¹H NMR: δ 1.29 (m, 8 H), 1.55 (m, 2 H, *J*=7.2 Hz), 1.97 (m, 2 H), 2.45 (m, 2 H), 3.49 (dd, 1 H, *J*=9.7 and 6.6 Hz), 3.64 (t, 2 H, *J*=6.6 Hz), 3.80 (s, 3 H), 4.86 (br s, 2 H), 5.36 (dt, 1 H, *J*=15.4 and 6.4 Hz), 5.49 (dt, 1 H, *J*=15.4 and 6.5 Hz), 6.83 (d, 2 H, *J*=8.7 Hz), 7.54 (d, *J*=8.7 Hz). ¹³C NMR: δ 25.3 (t), 28.2 (t), 28.7 (t), 32.0 (t), 34.7 (t), 42.7 (d), 55.2 (q), 62.9 (t), 114.7 (d), 117.5 (s), 126.1 (d), 134.0 (d), 138.1 (d), 160.4 (s), 176.8 (s).

(2Z,4E)-Dodeca-2,4-dien-12-olide (13). To a solution of lactone **10** (0.102 g, 0.267 mmol) in THF (3 ml), a 30% aqueous solution of H₂O₂ (0.3 ml) was added, and the mixture was stirred at ambient temperature for 3 h. Pentane (10 ml) was then added and the reaction mixture was neutralized with aqueous NaHCO₃. The organic layer was separated, dried (Na₂SO₄) and concentrated; the residue was subjected to column chromatography (5% Et₂O in pentane) to afford 0.047 g (91%) of dienolide **14** as white crystals, m.p. 38–39 °C, *R*_f 0.59 (EtOAc–

hexane = 2 : 8). $^1\text{H NMR}$: δ 1.42 (m, 4 H), 1.68 (m, 6 H), 2.25 (m, 2 H), 4.18 (m, 2 H), 5.56 (d, 1 H, $J_{2,3} = 11.1$ Hz), 6.11 (dt, 1 H, $J_{4,5} = 16.0$, $J_{5,6} = 4.3$ Hz), 6.64 (t, 1 H, $J_{2,3} = J_{3,4} = 11.1$ Hz), 7.30 (dd, 1 H, $J_{4,5} = 16.0$, $J_{3,4} = 11.1$ Hz). $^{13}\text{C NMR}$: δ 23.8 (t), 24.2 (t), 24.3 (t), 27.5 (t), 27.6 (t), 29.9 (t), 65.2 (t), 117.8 (d), 126.5 (d), 140.8 (d), 142.6 (d), 167.3 (s). Analysis: calc. for $\text{C}_{12}\text{H}_{18}\text{O}_2$: C, 74.19; H, 9.34. Found: C, 74.27; H, 9.45.

(*Z*)-Dodec-3-en-12-olide (**1**). A solution of dienolide **13** (0.040 g, 0.20 mmol) and (η^6 -naphthalene)tricarboxylchromium (0.25 g, 4.7 mmol) in THF (10 ml) was placed in a stainless steel autoclave under an atmosphere of argon. The vessel was sealed and filled/evacuated three times with H_2 (at 10 atm) to remove traces of O_2 . The hydrogen pressure was then adjusted to 40 atm, and hydrogenation was carried out at 45–50 °C for 2 h. The autoclave was rinsed with ether, and the resulting solution filtered and concentrated under reduced pressure. Column chromatography (using pentane containing 0 → 5% Et_2O as the eluent) gave 0.026 g (65%) of the title pheromone **1** as a colourless oil. $^1\text{H NMR}$ and $^{13}\text{C NMR}$ data were in close agreement with the literature.³

(2*E*,4*E*)-12-Hydroxydodeca-2,4-dienoic acid (**15**). Methyl (*E*)-12-hydroxy-2-(4-methoxyphenylseleno)dodec-4-enoate (**12a**) (0.221 g, 0.53 mmol) was treated with 30% H_2O_2 (0.3 ml) in THF (3 ml) as described for the preparation of compound **13**. Column chromatography (using pentane containing 5 → 40% EtOAc as the eluent) afforded 0.117 g (97%) of (2*E*,4*E*)-methyl 12-hydroxydodeca-2,4-dienoate as a yellowish oil. $^1\text{H NMR}$: δ 1.32 (m, 9 H), 1.42 (m, 2 H), 2.16 (q, 2 H, $J_{5,6} = J_{6,7} = 6.1$ Hz), 3.63 (t, 2 H, $J = 6.3$ Hz), 3.72 (s, 3 H), 5.78 (d, 1 H, $J = 15.6$ Hz), 6.12 (m, 2 H), 7.26 (dd, 1 H, $J = 15.6$ and 10.3 Hz). $^{13}\text{C NMR}$: δ 25.6 (t), 28.6 (t), 29.1 (t), 29.2 (t), 32.7 (t), 32.9 (t), 51.4 (q), 63.0 (t), 118.6 (d), 128.3 (d), 144.8 (d), 145.4 (d), 167.8 (s).

Saponification of the ester (0.117 g, 0.52 mmol) was then performed as described for the preparation of acid **8** to afford 0.100 g (92%) of the title compound as white crystals. $^1\text{H NMR}$: δ 1.33 (m, 8 H), 1.57 (m, 2 H), 2.18 (q, 2 H, $J_{5,6} = J_{6,7} = 5.8$ Hz), 3.64 (t, 2 H, $J = 6.6$ Hz), 5.40 (br s, 2 H), 5.78 (d, 1 H, $J = 15.4$ Hz), 6.19 (m, 2 H), 7.34 (dm, 1 H, $J = 15.4$ Hz).

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