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Synthesis and Characterization of the Four Geometrical Isomers of 3,5-Dodecadienyl Acetate

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Practical convergent syntheses of the four geometrical isomers of 3,5-dodecadienyl acetate are presented. These substances have been characterized by NMR and mass spectroscopy. (3*E*,5*Z*)-3,5-Dodecadienyl acetate is the main female sex pheromone component of the leaf roller *Bonagota cranaodes*, which is an important insect pest in apples in South America.

The isomeric 3,5-dodecadienyl acetates, as pure isomers and in defined mixtures, have been used as trap lures for flying insects in field screening experiments in Lithuania. Although no insects were found in the control traps, the numbers of males caught in the baited traps were not high enough to be statistically significant.

The economically most important insect pest on apples in South America is the leaf roller moth *Bonagota cranaodes* Meyrick (Lepidoptera: Tortricidae). The female sex pheromone of this moth has been identified as the 3*E*,5*Z*-isomer of dodecadienyl acetate.[1] Field tests have shown that traps baited with this attractant can be used to monitor the pest. Here we present the syntheses of the four geometric isomers of 3,5-dodecadienyl acetate (Schemes 1 and 2).

To establish whether any tortricids in the Northern hemisphere used these positional isomers, we launched a series of field experiments in Lithuania, in which we screened a forest for moths and other insects using 3,5-dodecadienyl acetate in their chemical communication. The results from this investigation are included in this publication.

Results and discussion

Syntheses. The (3*E*,5*Z*)-3,5-dodecadienyl and (3*E*,5*E*)-3,5-dodecadienyl acetates (Scheme 1) were synthesized via a Wadsworth–Horner–Emmons condensation reaction of methyl (*E*)-4-dimethylphosphono-2-butenoate (**2**) with octanal,[2] followed by a stereoselective low-temperature deconjugation of the resulting (2*E*,4*Z*)- and (2*E*,4*E*)-2,4-dodecadienoates (**3a** and **3b**) by LDA (which is a strong base of low nucleophilicity).[3] The deconjugated *E,Z* isomer **4a** was the major product. This procedure has been utilized in the synthesis of (3*E*,5*Z*)-3,5-tetradecadienoic acid[4] (=megatomic acid, the major sex pheromone component of the black carpet beetle, *Attagenus megatoma*[5]). Ikeda *et al.* (1987) suggest that the reason for the high *E,Z* selectivity is that the alkyl chain has a weaker steric interaction with the γ-proton in the conformer that, after deprotonation, yields the *E,Z* isomer, than the alkyl chain has with the delta proton in the conformer leading to the *E,E* isomer. A diisobutylaluminium hydride (DIBAH) reduction of the 3,5-dodecadienoates **4a** and **4b** yielded the corresponding alcohols and a subsequent acetylation gave the acetates **5a** and **5b**. The *E,Z* and *E,E* isomers were separated by liquid chromatography on silica gel impregnated with silver nitrate.

(3*Z*,5*Z*)-3,5-Dodecadienyl acetate was synthesized by a route involving a Cadiot–Chodkiewicz coupling reaction of 3-butyn-1-ol with 1-bromo-1-octyne (**6**) and dicyclohexylborane reduction of 3,5-dodecadiyn-1-ol (**7**) as the key steps (Scheme 2).[6]

(3*Z*,5*E*)-3,5-Dodecadienyl acetate was prepared by a reaction sequence involving the coupling reaction of 3-butyn-1-ol with (*E*)-1-octenyl iodide (**9**) in the presence of a catalytic amount of Pd $(PPh_3)_4$, using phase transfer conditions,[7] followed by a (*Z*)-stereoselective reduction of the triple bond in the (*E*)-enyne acetate **11**, using a Zn–Cu couple as the reducing agent (Scheme 2).[8]

Field results. Twenty-two males from 12 species belonging to five lepidopteran families were attracted by binary or

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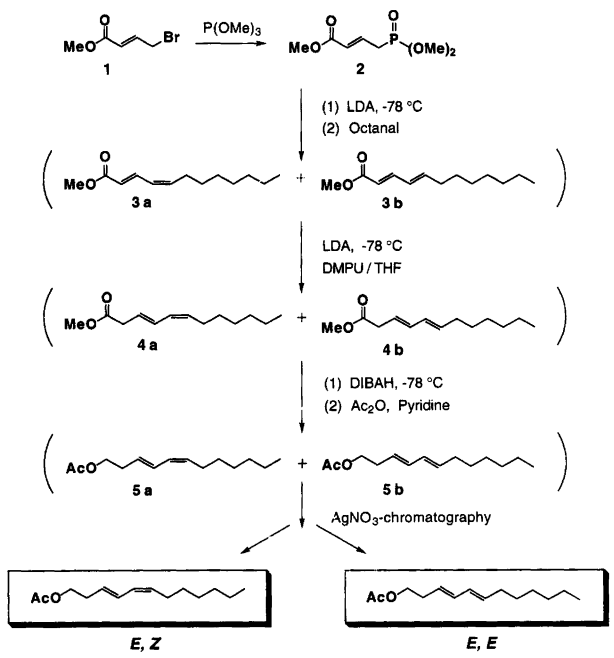
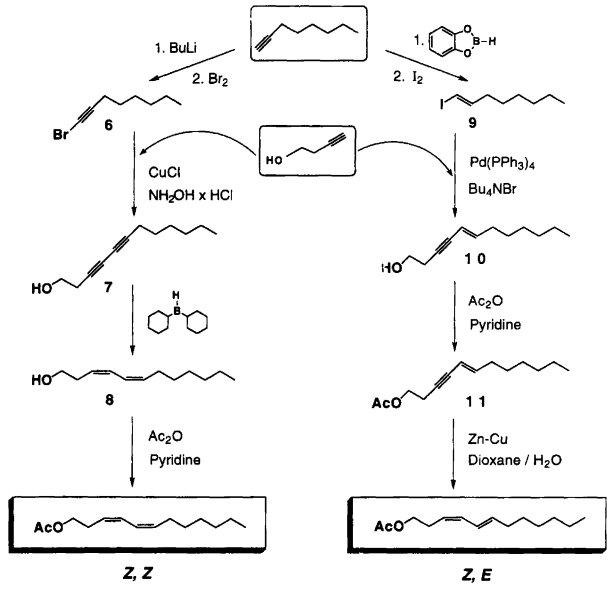


Scheme 1. Synthesis of the (*E,Z*)- and (*E,E*)-isomers of 3,5-dodecadienyl acetate.



Scheme 2. Syntheses of the (*Z,Z*)- and (*Z,E*)-isomers of 3,5-dodecadienyl acetate.

single component lures of the geometrical isomers. A 1:1 mixure of *E,E/Z,E* isomers caught three males of *Hypatima rhomboidella* (L.) [=*conscriptella* (Hb.)]. The *E,Z* isomer caught three male *Psoricoptera gibbosella* (Z.) and two males of *Recurvaria leucatella* (Cl.) while the *Z,Z* isomer caught two male *Argyresthia goedartella* (L.). Single male specimens of the following species were caught: *Brachmia rufescens* (Hw.), *Hypena proboscidaes* (L.), *Udea lutealis* (Hb.), *Udea prunalis* (Den. et Schiff.), *Archips rosana* (L.), *Hedya nubiferana* (Hw.) [=*dimidioalbana* (Rtz.)] and *Rhopobota naevana* (Hb.) [=*unipunctata* (Hw.)].

Almost half of the males attracted belonged to the family Gelechiidae. No catches by any of the tested lures differed significantly from the controls. However, the fact that only males were caught indicated a sex-selective attraction.

Experimental

The chemicals were obtained from Lancaster Synthesis Ltd or Aldrich. All reactions of air- and water-sensitive materials were performed under dry Ar. Liquid chromatography (LC) was carried out on silica gel (Merck 60, 0.040–0.063 mm) in 15 or 25 mm inner diameter (i.d.) glass columns. Gradient elution with hexane and increasing amounts of ethyl acetate was carried out as described by Baeckström *et al.*[9] TLC was performed on silica gel (Merck 60, HF precoated aluminium foil) using 40% ethyl acetate in hexane as the eluent. The plates were developed with vanillin and H_2SO_4 in ethanol. NMR spectra were recorded in $CDCl_3$ on an AM 400 spectrometer. Analytical GC was performed with an FID using a 30 m DB-WAX fused silica capillary column.

GC–MS analyses. Mass spectra were recorded at 70 eV on a Finnigan SSQ 7000 GC–MS instrument connected to a Varian 3400 GC. Injections were made in the splitless mode for 30 s at 200 °C using helium as the carrier gas. That instrument was equipped with a DB-5 fused silica capillary column (J&W 30 m, i.d. 0.25 mm, film thickness 0.25 μm) programmed from 70 °C (hold 1 min) at 6 °C min^{-1} to 140 °C and at 3 °C min^{-1} to 200 °C. The elution order of the isomers was: *EZ*, *ZE*, *ZZ* and *EE*.

Synthesis of (3E,5Z)- and (3E,5E)-3,5-dodecadienyl acetate. Methyl (2E)-4-dimethylphosphone-2-butenoate (**2**). The brominated methyl crotonate **1** (35.8 g, 0.20 mol) was added dropwise to trimethyl phosphite (27.3 g, 0.22 mol) at 120 °C (Scheme 1). The mixture was stirred for 0.5 h, while the methyl bromide formed was distilled off. The reaction mixture was allowed to cool and then diluted with methylene chloride (300 ml). Silica gel (200 g) was added, the methylene chloride evaporated off and the resulting gel was put on a column. Gradient chromatography (increasing amounts of methanol in methylene chloride) gave 39.5 g (95%) of product.

Methyl 2,4-dodecadienoates (**3a**) *and* (**3b**). Lithium diisopropylamide (LDA) was prepared by adding butyllithium (2.5 M in hexanes, 52.6 ml, 131 mmol) to diisopropylamine (13.3 g, 131 mmol) in 180 ml dry THF at <0 °C. The reaction mixture was cooled to −78 °C and the crotonate derivative **2** (25.8 g, 124 mmol) in dry THF (40 ml) was added. The mixture was then stirred for 1 h after which octanal (16.5 g, 129 mmol) was added. The cold bath was removed and the reaction mixture was stirred for 2 h before it was poured into sat.

NH_4Cl solution (100 ml). The organic phase was separated and the aqueous phase extracted with hexane (200 ml) and diethyl ether (2 × 150 ml). The combined organic phases were then dried with $MgSO_4$. After filtration the product was subjected to LC. The yield was 56% (14.5 g, 69.0 mmol) of an isomeric mixture consisting of **3a** and **3b** in the ratio 20:80 according to GC. The ratio varied between 7 and 20% **3a** from batch to batch. Slower addition of the methyl crotonate gave a lower temperature in the reaction vessel which in turn resulted in a smaller amount of **3a** formed in the reaction.

^{1}H NMR: *E,E*-isomer **3b**: δ 7.25 (dd, J=15.4, 9.9 Hz, 1 H), 6.16–6.12 (m, 2 H), 5.78 (d, J=15.4 Hz, 1 H) 3.73 (s, 3 H), 2.16 (q, J=6.7 Hz, 2 H), 1.42 (m, 2 H), 1.28 (m, 8 H), 0.88 (t, J=6.9 Hz, 3 H). ^{13}C NMR: δ 167.7, 145.4, 145.0, 128.3, 118.6, 51.4, 33.0, 31.8, 29.12, 29.07, 28.7, 22.6, 14.1. MS *m/z* (% relative intensities): 210 (*M*, 35), 111 (100), 81 (68), 93 (53), 82 (44), 79 (40), 67 (34), 179 (25), 136 (24), 100 (22).

^{1}H NMR: *E,Z*-isomer **3a**: δ 7.60 (dd, J=15.0, 11.3 Hz, 1 H), 6.12 (t, J=11.3 Hz, 1 H), 5.87 (m, 2 H), 3.73 (s, 3 H), 2.27 (q, J=6.8 Hz, 2 H), 1.42–1.28 (m, 10 H), 0.88 (t, J=6.9 Hz, 3 H). ^{13}C NMR: δ 167.4, 141.5, 139.5, 126.2, 120.5, 51.2, 31.4, 29.2, 29.0, 28.0, 26.7, 21.9, 13.6. MS *m/z* (% relative intensities): *E,Z*-isomer **3a:** 210 (*M*, 10), 111 (100), 81 (18), 79 (17), 67 (11), 113 (11), 100 (9), 179 (8), 139 (6).

Methyl 3,5-dodecadienoates (**4a**) *and* (**4b**). LDA was prepared by adding butyllithium (2.5 M in hexanes, 23 ml, 57 mmol) to diisopropylamine (6.07 g, 60 mmol) in THF (45 ml) at −40 °C. The mixture was stirred for 1 h after which the temperature was decreased to −70 °C and the two methyl 2,4-dodecadienoates (11 g, 52 mmol) in *N,N'*-dimethylpropyleneurea (DMPU) (40 ml) were added dropwise over 1 h at −70 °C. After being stirred for 1 h, the cold reaction mixture was poured into aqueous NH_4Cl–ice (150 ml), extracted with hexane (4 × 120 ml), dried ($MgSO_4$), concentrated and subjected to LC. The yield was 9.36 g (85%) of (3*E*,5*Z*)-3,5-dodecadienoate, containing between 2 and 10% of the *E,E*-isomer.

*(3*E,5*Z)- and (3*E,5*E)-3,5-Dodecadienols.* Methyl (3*E*,5*Z*)- and (3*E*,5*E*)-dodecadienoates (in all 3.17 g, 15.1 mmol) were dissolved in dry hexane (120 ml) and DIBAH (1 M, 31 ml, 31 mmol) in toluene was added at −5 to −10 °C over 0.5 h. After being stirred for 3.5 h the reaction was quenched with Baeckström reagent (10 g of Celite–Na_2SO_4, 1:1 by volume). The reaction mixture was filtered and washed with aqueous NH_4Cl (100 ml) and water (100 ml). The aqueous phases were extracted with hexane (100 ml) and ethyl acetate (120 ml). The combined organic phases were dried ($MgSO_4$), concentrated and subjected to LC. The yield of 3,5-dodecadienols varied between 57 and 86%.

MS *m/z* (% relative intensities), *E,Z*-isomer: 182 (*M*, 30) 67 (100), 79 (52), 81 (44), 95 (33), 41 (32), 109 (18), 151 (3). *E,E*-isomer: 182 (*M*, 45), 67 (100), 81 (50), 79 (42), 95 (54), 43 (22), 109 (22), 151 (4).

*(3*E,5*Z)- and (3*E,5*E)-3,5-Dodecadienyl acetates* (**5a**) *and* (**5b**). The mixture of (3*E*,5*Z*)- and (3*E*,5*E*)-3,5-dodecadien-1-ols (1.58 g, 8.7 mmol) was stirred in acetic anhydride and pyridine (6 ml, 1:2 v/v) at 0 °C for 1 h and at room temperature for 2 h. Diethyl ether (120 ml) and hexane (250 ml) were then added and the reaction mixture was poured into ice-water (50 ml), washed with water (50 ml), dried ($MgSO_4$) and chromatographed on silica gel to give 1.85 g (95%) of a mixture of (3*E*,5*Z*)- and (3*E*,5*E*)-3,5-dodecadienyl acetates. Pure (3*E*,5*Z*)- and (3*E*,5*E*)-dodecadienyl acetates were obtained by LC on $AgNO_3$-impregnated silica gel (15% w/w).

*(3*E,5*Z)-3,5-Dodecadienyl acetate* (**5a**). ^{1}H NMR: δ 6.38 (ddd, J=15.3, 11.0, 1.3 Hz, 1 H), 5.94 (dd, J=11.0, 11.0 Hz, 1 H), 5.60 (dt, J=15.2, 7.0 Hz, 1 H), 5.37 (dt, J=10.8, 7.6 Hz, 1 H), 4.11 (t, J=6.8 Hz, 2 H), 2.42 (q, J=6.8 Hz, 2 H), 2.15 (q, J=7.0 Hz, 2 H), 2.04 (s, 3 H), 1.42–1.23 (m, 8 H), 0.88 (t, J=6.9 Hz, 3 H). ^{13}C NMR: δ 171.1, 131.6, 128.6, 128.2, 128.1, 63.8, 32.1, 31.7, 29.6, 28.9, 27.7, 22.6, 21.0, 14.1. MS *m/z* (% relative intensities): 224 (*M*, 0), 80 (100), 79 (92), 43 (43), 164 (38), 93 (25), 78 (19), 91 (18), 110 (10), 61 (0).

*(3*E,5*E)-3,5-Dodecadienyl acetate* (**5b**). ^{1}H NMR: δ 6.06 (ddd, J=14.7, 10.4, 1.0 Hz, 1 H), 6.01 (ddd, J=14.7, 10.4 Hz, 1 H), 5.62 (dt, J=14.7, 7.0 Hz, 1 H), 5.50 (dt, J=14.7, 7.0 Hz, 1 H), 4.09 (t, J=6.8 Hz, 2 H), 2.38 (q, J=6.8 Hz, 2 H), 2.05 (q, J=7.0 Hz, 2 H), 2.04 (s, 3 H), 1.42–1.23 (m, 8 H), 0.88 (t, J=6.9 Hz, 3 H). ^{13}C NMR: δ 171.1, 134.0, 133.0, 129.8, 126.3, 63.9, 32.6, 31.9, 31.7, 29.3, 28.9, 22.6, 21.0, 14.1. MS *m/z* (% relative intensities): 224 (*M*, 0), 80 (100), 79 (90), 43 (30), 164 (25), 41 (25), 93 (22), 123 (5), 111 (2), 61 (0).

Synthesis of (3Z,5Z)-3,5-dodecadienyl acetate. 1-Bromo-1-octyne (**6**). 1-Octyne (4.4 g, 40 mmol) in diethyl ether (50 ml) was added slowly to a THF solution of butyllithium (40 mmol) at −50 °C over 15 min. The reaction mixture was then cooled to below −70 °C and stirred vigorously, while bromine (6.4 g, 40 mmol) was added dropwise over 1 h. The temperature was allowed to rise to room temperature before the reaction mixture was poured into ice–water (100 ml), extracted with hexane and dried ($MgSO_4$). Distillation gave 5.42 g of 1-bromo-1-octyne, b.p. 72–75 °C/ 13 mmHg (72% yield). ^{1}H NMR: δ 2.19 (t, J=7.1 Hz, 2 H), 1.51 (quintet, J=7.1 Hz, 1 H), 1.41–1.37 (m, 2 H), 1.36–1.24 (m, 5 H), 0.89 (t, J=6.9 Hz, 3 H).

3,5-Dodecadiyn-1-ol (**7**). A solution of cuprous chloride (75 mg) and hydroxylamine hydrochloride (0.5 g) in methanol (10 ml) was added to a stirred solution of butylamine in water (60%, 5 ml). A solution of 3-butyn-1-ol (0.8 g, 11 mmol) in methanol (5 ml) was added

rapidly and a yellow suspension was formed. 1-Bromo-1-octyne (1.89 g, 10 mmol) in methanol (10 ml) was added dropwise at room temperature over 2.5 h. The reaction mixture was stirred at room temperature for 3 h, then treated with potassium cyanide (0.25 g) and ammonium chloride (1 g) in water (60 ml), extracted with hexane (4 × 100 ml) and dried ($MgSO_4$). Concentration *in vacuo* followed by chromatography yielded 1.51 g (85%) of 3,5-dodecadiyn-1-ol. ^{1}H NMR: δ 3.73 (t, J=6.2 Hz, 2 H), 2.53 (t, J=6.2 Hz, 2 H), 2.24 (t, J=7.0 Hz, 2 H), 1.55–1.48 (m, 8 H), 1.42–1.19 (m, 8 H), 0.88 (t, J=6.9 Hz, 3 H). ^{13}C NMR: δ 78.4, 73.6, 67.2, 64.9, 60.9, 31.3, 28.5, 28.2, 23.6, 22.5, 19.1, 14.0.

Dicyclohexylborane. The temperature was kept between −5 and −10 °C, while a solution of borane in tetrahydrofuran (1 M, 20 ml, 20 mmol) was added slowly over a period of 30 min to a solution of cyclohexene (3.29 g, 40 mmol) in THF (20 ml). The resultant milky solution was stirred at 0 to −10 °C for 2 h and then used as such in the next step.

(3Z,5Z)-3,5-Dodecadien-1-ol (**8**). A solution of 3,5-dodecadiyn-1-ol (1.6 g, 9 mmol) in THF (15 ml) was added dropwise below 0 °C to the above dicyclohexylborane solution (20 mmol). The suspension was stirred at approximately −5 °C for 2 h and then allowed to reach room temperature After 2 h of stirring at room temperature the precipitate of the dicyclohexylborane disappeared. Glacial acetic acid (5 ml) was then added and the mixture was stirred overnight at 45 °C. Oxidation of the resulting dicyclohexylborinate was achieved by addition of sodium hydroxide (6 M, 20 ml) followed by dropwise addition of hydrogen peroxide (35%, 6 ml) at a rate maintaining the reaction mixture at 30–35 °C. The mixture was stirred for an additional 30 min and was then poured into ice–water (60 ml), extracted with hexane (4 × 100 ml), dried ($MgSO_4$) and chromatographed to give 3.32 g of a mixture of (3*Z*,5*Z*)-3,5-dodecadien-1-ol and cyclohexanol. This mixture was then used in the next reaction step.

(3Z,5Z)-3,5-Dodecadienyl acetate. The mixture of (3*Z*,5*Z*)-3,5-dodecadien-1-ol and cyclohexanol (3.32 g) thus obtained was stirred in acetic anhydride and pyridine (12 ml, 1 : 2 v/v) at 0 °C for 1 h and at room temperature for 2 h. The reaction mixture was then poured into 30 ml of ice–water, extracted with hexane (4 × 100 ml), dried over $MgSO_4$ and chromatographed on silica gel to give 2.5 g of a mixture: 30% (3*Z*,5*Z*)-3,5-dodecadienyl acetate, 2% (3*E*,5*Z*)-3,5-dodecadienyl acetate and 68% cyclohexyl acetate. Pure (99%) (3*Z*,5*Z*)-3,5-dodecadienyl acetate was obtained by LC on $AgNO_3$-impregnated silica gel. The yield of the *Z,Z*-isomer from **7** was 37% after the two final reaction steps. ^{1}H NMR: δ 6.37 (dd, J=11.7, 10.8 Hz, 1 H), 6.21 (dd, J=11.0, 11.4 Hz, 1 H), 5.50 (dt, J=10.8, 7.6 Hz, 1 H), 5.39 (dt, J=10.8, 7.6 Hz, 1 H), 4.10 (t, J=6.9 Hz, 2 H), 2.51 (q, J=7.0 Hz, 2 H), 2.16 (q, J=7.4 Hz, 2 H), 2.04 (s, 3 H), 1.42–1.28 (m, 8 H), 0.88 (t, J=6.9 Hz, 3 H). ^{13}C NMR: δ 171.1, 133.6, 126.2, 125.8, 123.0, 63.7, 31.7, 29.5, 28.9, 27.5, 27.0, 22.6, 21.0, 14.1. MS *m/z* (% relative intensities): 224 (*M*, 0), 79 (100), 80 (95), 164 (85), 32 (28), 93 (24), 43 (20), 91 (19), 77 (18), 61 (0).

Synthesis of (3Z,5E)-3,5-dodecadienyl acetate. (E)-1-Octenyl iodide (**9**). Catecholborane (3.6 g, 30 mmol) was added in one portion to 1-octyne (3.3 g, 30 mmol) and the mixture was stirred at 70 °C for 2 h. The reaction mixture was then cooled to room temperature and water (30 ml) was added. After 2 h and cooling to 0 °C the (*E*)-octenylboronic acid obtained by the hydrolysis was collected by filtration. It was washed several times with water to remove traces of catechol. The (*E*)-octenylboronic acid was then dissolved in 30 ml of ether and cooled to 0 °C. Aqueous sodium hydroxide (3 M NaOH, 30 ml) and iodine (9.14 g, 36 mmol) in ether (90 ml) were added sequentially. The stirring was continued for 0.5 h before a solution of sodium thiosulfate was added to destroy the excess of iodine. The ether solution was separated and the aqueous phase extracted with hexane (2 × 100 ml). The combined organic phases were then dried ($MgSO_4$) and concentrated *in vacuo.* Liquid chromatography yielded 3.69 g (52%) of (*E*)-1-octenyl iodide. ^{1}H NMR: δ 6.51 (dt, J=14.3, 7.2 Hz, 1 H), 5.97 (dt, J=14.3, 1.4 Hz, 1 H), 2.0 (dq, J=7.3, 1.4 Hz, 1 H), 1.42–1.34 (m, 2 H), 1.38–1.22 (m, 6 H), 0.88 (t, J=6.9 Hz, 3 H). ^{13}C NMR: δ 146.8, 74.2, 36.0, 31.6, 28.6, 28.3, 22.6, 14.0.

(E)-5-Dodecen-3-yn-1-ol (**10**). A mixture of (*E*)-1-octenyl iodide (3.65 g, 15.3 mmol) and 3-butyn-1-ol (1.07 g, 15.3 mmol) in benzene (2 ml) was added to a mixture of CuI (29 mg, 0.15 mmol), tris(dibenzylideneacetone)-dipalladium(0) (140 mg, 0.15 mmol) and tetrabutylammonium bromide (49 mg, 0.15 mmol) in benzene (4 ml). Aqueous NaOH (10%, 17 ml) was then added and the resulting mixture was stirred at room temperature for 22 h. TLC-check of the reaction mixture revealed that the reaction proceeded very slowly. Therefore, Pd $(PPh_3)_4$ (100 mg, 0.11 mmol) and tetrabutylammonium bromide (100 mg, 0.31 mmol) were added and the mixture was stirred overnight. It was then poured into ice–water (50 ml) and extracted with hexane (4 × 100 ml). After drying ($MgSO_4$) and concentration, the organic residue (3.07 g) was diluted with hexane (80 ml), cooled in ice and filtered. The filtrate was concentrated and chromatographed on silica gel to give 0.46 g of (*E*)-5-dodecen-3-yn-1-ol and 1.6 g recovered (*E*)-1-octenyl iodide. The yield was 30% based on converted alkenyl iodide. ^{1}H NMR: δ 6.10 (dt, J=15.8, 7.1 Hz, 1 H), 5.45 (dqv, J=15.9, 1.8 Hz, 1 H), 4.11 (q, J=7.2 Hz, 1 H), 3.72 (t, J=6.2 Hz, 2 H), 2.57 (td, J=6.2, 2.0 Hz, 2 H), 2.08 (q, J=6.9 Hz, 2 H), 2.04 (s, 3 H), 1.42–1.22 (m, 8 H), 0.88 (t, J=6.9 Hz, 3 H). ^{13}C NMR: δ 144.6,

109.3, 84.5, 81.3, 61.2, 33.0, 31.6, 28.8, 28.7, 23.8, 22.6, 14.1.

(E)-5-Dodecen-3-yn-1-yl acetate (**11**). (*E*)-5-Dodecen-3-yn-1-ol (0.2 g, 1.1 mmol) was stirred in acetic anhydride and pyridine (3 ml, 1:2 v/v) at 0 °C for 1 h and at room temperature for 2 h. The reaction mixture was poured into ice–water (20 ml), extracted with hexane (4 × 50 ml), dried ($MgSO_4$) and chromatographed to give 0.24 g of (*E*)-5-dodecen-3-ynol acetate in 97% yield. MS *m/z* (% relative intensities): 222 (*M*, 0), 43 (100), 78 (95), 91 (40), 162 (25), 65 (17), 41 (15), 79 (15), 39 (14), 61 (0).

(3Z,5E)-3,5-Dodecadienyl acetate. Cupric chloride (0.44 g, 3.28 mmol) was dissolved in hot water (4 ml) and Zn-powder (1.76 g, 26.8 mmol) in hot water (4 ml) was added in one portion. The catalyst formed was washed with hot water and one quarter of it was added to a solution of (*E*)-5-dodecen-3-yn-1-yl acetate (0.24 g, 1.1 mmol) in dioxane–water (1:1, 4 ml). This mixture was heated at 80 °C for 28 h while the remaining catalyst was added in three portions. The reduction was monitored by GC. When the reaction was complete, the catalyst was filtered off and rinsed with hexane. The filtrate was washed with water, and the aqueous phase was re-extracted with hexane. The combined organic phases were then dried with $MgSO_4$, concentrated and subjected to LC. The yield was 87% (0.21 g) of (3*Z*,5*E*)-3,5-dodecadienyl acetate, contaminated by 1.2% of the *Z,Z*-isomer, 0.2% of the *E,E*-isomer and 1.2% of (*E*)-5-dodecen-3-yn-1-ol. *Argentum* chromatography increased the purity to 99.2%. ^{1}H NMR: δ 6.27 (dd, J=15.0, 11.0 Hz, 1 H), 6.06 (dd, J=10.9, 10.9 Hz, 1 H), 5.71 (dt, J=15.0, 7.0 Hz, 1 H), 5.26 (dt, J=10.7, 7.6 Hz, 1 H), 4.09 (t, J=6.9 Hz, 2 H), 2.50 (q, J=6.9 Hz, 2 H), 2.10 (q, J=7.5 Hz, 2 H), 2.04 (s, 3 H), 1.42–1.27 (m, 8 H), 0.88 (t, J=6.9 Hz, 3 H). ^{13}C NMR: δ 171.1, 136.3, 131.4, 125.1, 123.7, 63.8, 32.9, 31.7, 29.3, 28.9, 27.2, 22.6, 21.0, 14.1. MS *m/z* (% relative intensities): 224 (*M*, 0), 80 (100), 79 (96), 164 (84), 93 (22), 43 (19), 91 (19), 77 (18), 110 (6), 61 (0).

Field tests. Ethanol-washed grey halobutyl rubber septa (Thomson Scientific, USA) were loaded with test chemicals absorbed as heptane solutions (HPLC grade). Each septum was fixed inside an opaque white delta trap (from Flora Co., Tartu, Estonia). The field tests were carried out in the vicinity of Vilnius (Eastern Lithuania) in a mixed forest from July 14 to September 15, 1997.

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