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Methyl (2*E*,4*Z*,6*Z*)-Deca-2,4,6-trienoate, a Thermally Unstable, Sex-Specific Compound from the Stink Bug *Thyanta pallidovirens.*

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Abstract: Sexually mature male stink bugs, *Thyanta pallidovirens*, release a male-specific blend of volatiles, including several sesquiterpene hydrocarbons, and the highly conjugated ester methyl (2*E*,4*Z*,6*Z*)-deca-2,4,6-trienoate **1**. The latter compound was synthesized, and found to rearrange under GC conditions via a 1,7 sigmatropic rearrangement. © 1997 Elsevier Science Ltd.

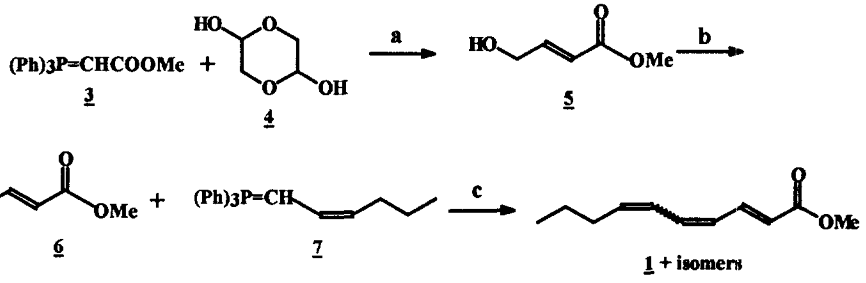
In studies of the semiochemistry of the stink bug *Thyanta pallidovirens*, headspace sampling revealed that sexually mature males produce a group of sex-specific compounds, including the sesquiterpenes zingiberene, curcumene, and sesquiphellandrene. Gas chromatograms also consistently showed a broad peak of irregular shape, eluting before the cluster of sesquiterpenes on a nonpolar DB-5 column. Successive mass spectra showed molecular ions at *m/z* 180, but the spectra varied across the peak, suggesting that the peak was composed of a mixture of compounds, or that a single compound was rearranging under the GC conditions.

Hydrogenation of the crude extract resulted in the disappearance of the unknown peak, and the appearance of a peak with *m/z* 186, identified as methyl decanoate by comparison with an authentic standard. This suggested that the unknown was a triunsaturated ester; the analogous methyl (2*E*,4*Z*)-deca-2,4-dienoate **2** is a known pheromone component for several stink bug species.[1]

HPLC analysis (150 x 3 mm, 5 μ LC-Si silica column, 0.5% THF in hexane) of the crude extract determined that the unknown was indeed a single compound, with a UV maximum (302 nm) at considerably longer wavelength than the diene analog **2** (λ_{max} =256 nm, hexane) confirming that the unknown was a fully conjugated triene ester. Approx. 2 mg of the unknown were isolated from a combined extract of several thousand bug-hours of headspace volatiles by HPLC, and ^{1}H and ^{1}H-^{1}H COSY NMR spectra unequivocally determined the compound to be methyl (2*E*,4*Z*,6*Z*)-deca-2,4,6-trienoate **1**.[2] The rearrangement of this isomer on heating is apparently due to a 1,7 sigmatropic rearrangement yielding the deconjugated (3*Z*,5*Z*,7*E*)-isomer, as previously described for the (2*E*,4*Z*,6*Z*)-undecatrienoate analog.[3]

In our first synthesis of 1 (Scheme 1), reaction of carbomethoxymethylene triphenylphosphorane **3** with 2,5-dihydroxy-1,4-dioxane **4** (benzene, reflux 5 h)[4], followed by Swern oxidation[5] gave unsaturated aldehyde **6** (48%). Wittig reaction of phosphorane 7 from addition of LDA to (2*Z*)-hexenyltriphenylphosphonium bromide with aldehyde **6** in ether at 0°C gave a mixture of isomers which were separable only with difficulty by HPLC, and so this route was not pursued.

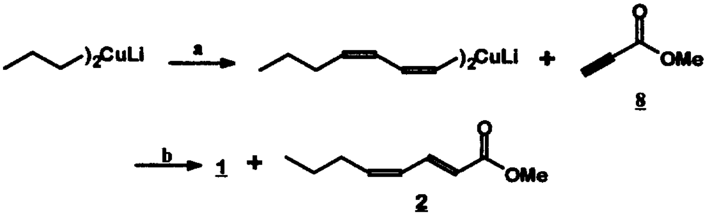
Scheme 1



a) Benzene, reflux; b) Swern oxidation; c) ether, 0°C.

A one-pot, stereospecific synthesis, featuring two sequential carbocuprations of acetylene, was more useful, providing exclusively the (2*E*,4*Z*,6*Z*)- isomer, albeit in low yield, and contaminated with the (2*E*,4*Z*)-diene analog (Scheme 2).[3] Thus, propyllithium in hexanes (40 mmol) was added to a slurry of $CuBrMe_2S$ (20 mmol) in ether at -40°C. After stirring 30 min at -30°, the mixture was cooled to -50° and acetylene (44 mmol) was bubbled in over 10 min. The mixture was warmed to -25° and stirred 30 min, then warmed to -10°, and a second acetylene addition was made (88 mmol) over 20 min. The mixture was then cooled to -78°, and methyl propiolate **8** (20 mmol) in THF was added dropwise. After stirring 30 min, the reaction was quenched with saturated aq. NH_4Cl in 2M HCl and worked up, producing a ~1:3 mixture of trienoate 1 with dienoate **2**. The mixture was readily separable by reverse phase flash chromatography (70% MeOH in water), providing stereochemically pure 1 (13%).

Scheme 2



a) Excess acetylene, -50 to -10°C,ether; b) -78°C, 30 min.

The function of this compound, alone or in combination with the other male-specific compounds, is under investigation. It elicited strong responses from female antennae in electroantennographic trials, supporting a pheromonal role, particularly as the analog (2*E*,4*Z*)-deca-2,4-dienoate is a known stink bug pheromone. Moreover, during the course of these investigations, the thermally stable (2*E*,4*E*,6*Z*)- isomer was identified as a male-produced pheromone of the stink bug *Plautia stali*.[6]

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2. ^{1}H NMR (500 MHz, $CDCl_3$): δ7.78 (dd, 1H, J=15.2, 12.2 Hz; H_3), 6.60 (m, 2H; H_5, H_6), 6.09 (br. t, 1H, J=11.7, 9.7 Hz; H_4), 5.89 (d, 1H, J=15.2 Hz; H_2), 5.73 (br. quart, 1H, J=7.7 Hz; H_7), 3.75 (s, 3H; OMe), 2.21 (br. quart, 2H, J=7.4 Hz; H_8), 1.44 (septet, 2H, J=7.4 Hz; H_9), 0.92 (t, 3H, J=7.4 Hz; H_{10}). ^{13}C NMR: δ 167.54, 139.30, 137.40, 132.5, 125.89, 123.29, 121.06, 51.54, 29.72, 22.61, 13.72.
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