Identification and Electrophysiological Activity of a Novel Hydroxy Ketone Emitted by Male Cereal Leaf Beetles

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Comparisons of collections of volatiles from male and female *Oulema melanopus*, feeding on host foliage (oats), revealed an electrophysiologically active male-specific compound, (*E*)-8-hydroxy-6-methyl-6-octen-3-one (**7**), which is a new natural product. The structure of **7** was elucidated by spectroscopic and microchemical studies and confirmed by chemical synthesis. Antennal electrophysiology showed the sensitive detection of **7** by both sexes, which is consistent with a male-produced aggregation pheromone.

The cereal leaf beetle, *Oulema melanopus* L. (Coleoptera: Chrysomelidae), is a serious pest of wheat, oats, and barley.[2] Originally from Europe and Asia, the beetle was first found in the United States in southwestern Michigan in 1962 and slowly expanded its range to include most States east of the Mississippi River.[3] Recently, damaging populations have been reported in the Middle Atlantic states and some Western states.[4] Current control efforts are focused primarily on the introduction of imported natural enemies. The beetles overwinter as adults and emerge in the spring when its hosts are most succulent. Adults are reproductively active during this time, and mating and oviposition occur throughout the spring and early summer. The larvae feed on the leaves and pupate in the soil. Newly emerged adults appear in late summer and early fall, but no mating occurs during this period. During the spring, feeding adults likely use chemical signals (semiochemicals) for mate location. However, the chemical communication of the cereal leaf beetle is unstudied, and there is only a limited amount of basic pheromone knowledge available for beetles belonging to the Chrysomelidae, a large and important family. So far, the only identified chrysomelid pheromones are the female-produced pheromones in the genus *Diabrotica*[5] and the male-produced pheromone of the flea beetle *Phyllotreta cruciferae* Goeze.[6,7]

Pest control efforts could benefit from an attractant for cereal leaf beetles for detection and monitoring of new pest infestations. This study was designed to detect and identify possible semiochemicals used in the chemical communication of the cereal leaf beetle, and a likely pheromone candidate was isolated, identified, and synthesized.

Results and Discussion

GC comparison of volatiles collected from male and female *O. melanopus* feeding on oat plants revealed a male-specific compound (Figure 1). This compound could also be detected, in various amounts, with grouped males or mixed sex groups, but not with single or grouped females. This male-specific compound was absent in whole body extracts or volatiles collected from male insects without the presence of the oat plant. The unlabeled peaks in Figure 1 were primarily oat volatiles, based on GC−MS comparisons to uninfested plant material and synthetic standards. The total amount of the male-specific compound emitted per male per day was 6.3 ± 7.9 ng (± SD, $N = 22$), with several males emitting as much as 20 ng/day ($N = 2$). Fifty out of a total of 177 male volatiles collections showed the presence of the sex-specific compound. This variability might have been due to the lack of feeding during some of the volatiles collections because the majority of those collections that did not show the male-specific compound were also without noticeable feeding damage. The male-specific compound eluted from an open silica column with ether, but not with 25% ether in hexane, suggesting a relatively polar oxygenated compound.

The molecular formula of the male-specific compound was determined from mass spectral data. The EIMS of the natural material is presented in Figure 2, upper panel. Examination of single-ion chromatograms indicated that the weak ion at *m*/*z* 156 (0.14% of base peak) was in fact part of the spectrum, and it was believed to be the molecular ion. No likely matches were found in a search of the MS library. Negative CIMS (methane) of the compound gave a base peak and highest mass peak at *m*/*z* 155, which supported a molecular weight of 156. The prominent peak at *m*/*z* 138 in the EIMS (M − 18, 6%) then represented loss of water. HREIMS indicated a formula of $C_9H_{14}O$ for the *m*/*z* 138 ion (observed 138.1031, calculated 138.1044); thus the molecular formula of the original compound was concluded to be $C_9H_{16}O_2$ (with two degrees of unsaturation). Positive CIMS data were consistent with this formula. With methane, the base peak was *m*/*z* 139 (M + 1 − 18), again showing ready loss of water. Softer ionization with isobutane also gave a base peak of *m*/*z* 139 and a higher mass peak at *m*/*z* 155 (M − 1, 7%); a primary alcohol standard (1-dodecanol) similarly produced M + 1 − 18 and M − 1 ions under these conditions.

The carbon skeleton and the location of one functional group were determined by chemical derivatization and mass spectrometry. Hydrogenation produced a compound with apparent molecular weight 142 (EIMS in Figure 2, lower panel). By HREIMS, the molecular formula was $C_9H_{18}O$ (observed 142.1362, calculated 142.1358). This formula indicated that hydrogenolysis had occurred (e.g., loss of one oxygen as water), and the decrease in GC retention time from 9.75 to 6.54 min was consistent with this. The formula also represented a net increase of two hydrogens, indicating saturation of a double bond or ring cleavage.

The hydrogenation product was not in the MS library, but the search suggested various 3-alkanones (the fragment

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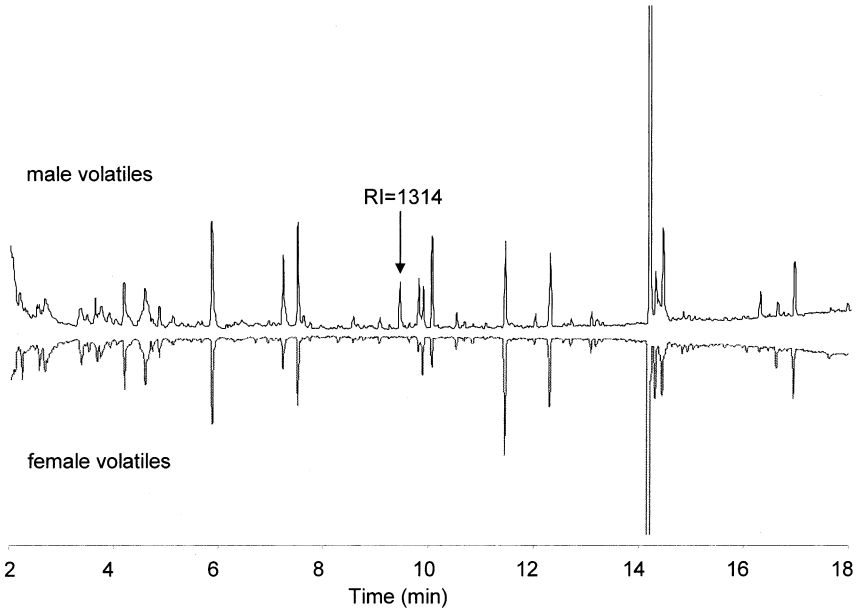


Figure 1. Gas chromatographic comparison of volatiles collected from male and female *O. melanopus* feeding on oat seedlings. Arrow denotes the presence of a male-specific compound. Retention index (RI) is relative to *n*-alkanes on an EC-1 column.

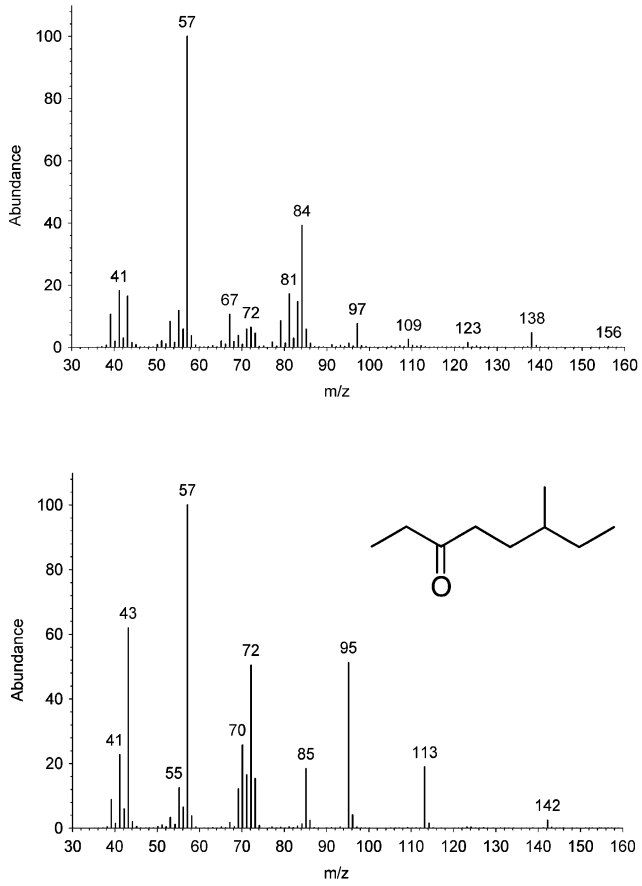


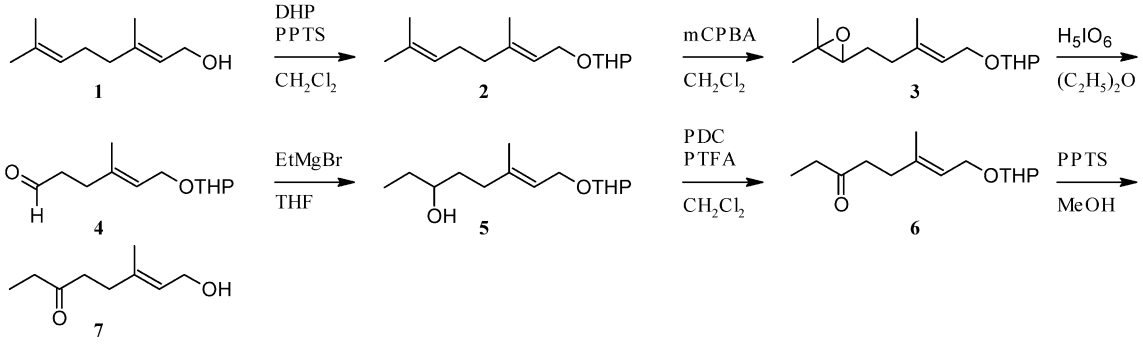
Figure 2. EI-mass spectrum of male-specific compound (upper) from *O. melanopus* and EI-mass spectrum of hydrogenation product (lower).

at *m*/*z* 72 would be due to a McLafferty rearrangement). Importantly, the peak at *m*/*z* 95 (M − 47, loss of ethyl and water) was far more intense in the hydrogenation product (56%) than in 3-nonanone (4%), the straight-chain ketone of the same molecular weight, and branching was suggested. The library lacked methyl-branched 3-octanones, but it did contain all possible methyl-branched 3-heptanones. Of these, only 6-methyl-3-heptanone gave an intense (30−60%) M − 47 peak (at *m*/*z* 81). By analogy, a likely structure for the hydrogenation product was 6-methyl-3-octanone. A literature search for this ketone revealed that it had been reported as a component of the alarm pheromones of ants in the genus *Crematogaster*[8] and as a minor component of the sex pheromone of the caddisfly *Hesperophylax occidentalis*,[9] and the published spectral data agreed well with those obtained here.

The hydrogenation product reacted with $LiAlH_4$, further supporting the presence of a keto group. As expected for the alcohol product, the reaction increased the GC retention time slightly, from 6.54 to 6.62 min, and although the EIMS of the product did not show a molecular ion, a peak was seen at *m*/*z* 126 (M − H_2O, 1%). Other significant ions were at *m*/*z* 115 (27%), 97 (81%), 84 (4%), 69 (27%), 57 (100%), 55 (71%), and 41 (25%). These reactions and publications defined the underlying 6-methyl-3-octanone structure but still left ambiguity about the location and nature of the second oxygen and the remaining degree of unsaturation.

Enough material (8 μg) was eventually accumulated and purified (HPLC, 15% acetone in hexane) for proton NMR, and this study defined the position of a double bond and hydroxyl group. The proton spectra of the natural and synthetic compounds are shown in Figure 3. Major features were one aliphatic and one olefinic methyl signal (H1 and H6a, respectively), one olefinic proton (H7), and two methylene protons (H8) that, by shift, were probably geminal to an OH function. An ethyl group adjacent to the keto group is represented by H1 (3H) and H2 (2H, J = 7.3, coupling clear in COSY spectrum). On the other side of the keto group were two methylene signals (H4 and H5) that were strongly coupled to each other in the COSY spectrum ($J \cong 7$). The shift of H5 (δ 2.18) suggested it was adjacent to a double-bond carbon, but it was not split by the olefinic proton H7 (although it was probably broadened by the protons near the olefinic system). From the COSY spectrum, olefinic proton H7 was strongly coupled to methylene H8 (J = 6.4) and weakly coupled to olefinic methyl H6a (J = 1.3). These spectral features defined a primary alcohol that is allylic to a trisubstituted double bond and led, combined with all other spectral information, to the tentative assignment of 8-hydroxy-6-methyl-6-octen-3-one (**7**) as the structure of the male-specific compound.

Scheme 1. Synthesis of (*E*)-8-hydroxy-6-methyl-6-octen-3-one (see text for abbreviations)



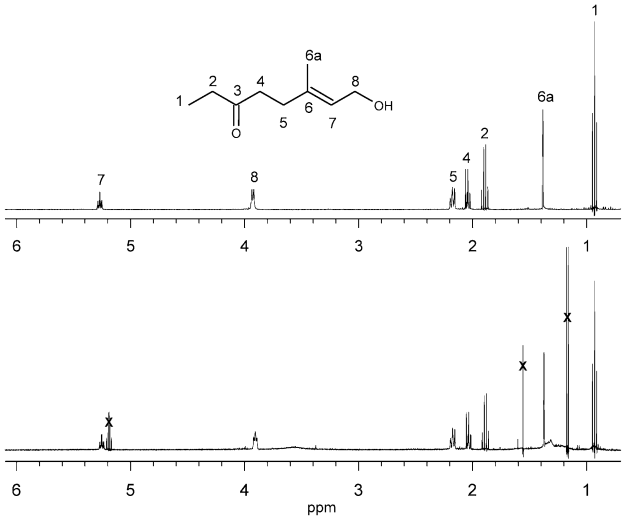


Figure 3. Proton NMR spectra of synthetic (*E*)-8-hydroxy-6-methyl-6-octen-3-one (upper) and natural (*E*)-8-hydroxy-6-methyl-6-octen-3-one obtained from *O. melanopus* males (lower) and in benzene-d_6. Impurity peaks in lower spectrum are denoted by X; see text.

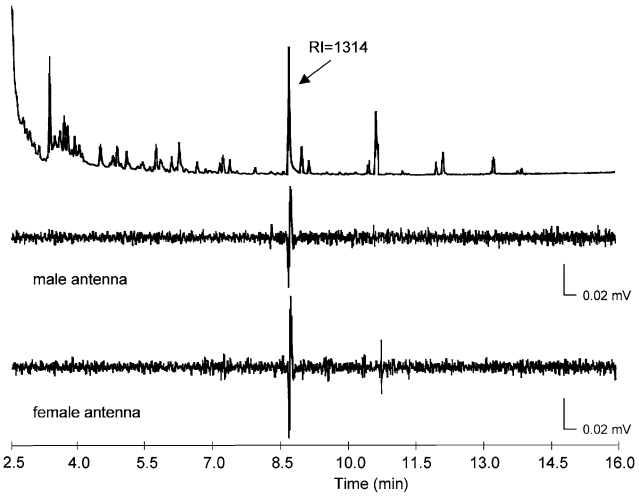


Figure 4. Simultaneously recorded gas chromatogram (GC) and electroantennogram responses (EAD) of male and female antenna to volatiles collected from 5 male *O. melanopus* feeding on oat seedlings. Arrow denotes the presence of natural **(***E***)**-8-hydroxy-6-methyl-6-octen-3-one.

The identification of **7**, including the *E* configuration of the double bond, was confirmed by a six-step chemical synthesis (Scheme 1). The approach was to prepare the *E*-isomer using geraniol as a convenient starting material, having one double bond, hydroxyl functional group, and the needed methyl branch, all in proper positions. The *E*-isomer was the first target because it was likely to be the more stable isomer. If the product had not matched the natural material, the synthesis would have been repeated with the *Z* alcohol nerol as starting material. The hydroxyl group was protected as THP ether,[10] followed by selective epoxidation.[11] The epoxide was cleaved to the aldehyde,[12] followed by a Grignard addition,[13] oxidation,[14] and removal of the THP group.[10] Synthetic **7** matched the natural male-derived compound exactly by mass spectrum and GC retention time.

As shown in Figure 3, the proton spectra of the natural and synthetic compounds were identical except for several impurity peaks and for the effect of water in one sample. In the natural sample, two impurity signals at 5.19 and 1.17 ppm were strongly coupled to each other in the COSY spectrum but not to any other signals; they were consistent with the trimer of acetaldehyde, which may have been present in the acetone HPLC solvent. A third impurity peak was at 1.56 ppm. The only real spectral difference between the natural and synthetic samples was that the signal at 3.93 ppm was a triplet in the natural sample but a doublet in the synthetic sample. The natural sample was apparently dry enough so that splitting from the hydroxyl proton could be observed; addition of D_2O to the natural sample collapsed the signal to a doublet.

Electrophysiological (GC-EAD) analysis of collected volatiles of male beetles feeding on oat leaves showed that the natural male-specific compound was detected by the antennae of both sexes (males $N = 5$, females $N = 14$) (Figure 4). Similar results were obtained for synthetic **7** (males $N = 7$, females $N = 5$). As expected from the GC−MS analysis, collected volatiles from oats and female-infested plant material did not show any antennal activity at the retention time observed for the male-specific compound. In addition, GC-EAD comparisons of combined and concentrated collected volatiles from oats and beetle-infested oats showed that male and female antennae responded to benzaldehyde, (*Z*)-3-hexenyl acetate, nonanal, and methyl salicylate verified by GC−MS with authentic standards (results not shown). However, the responses to these plant-derived compounds were weaker and therefore less consistent than the antennal activity for the male-specific compound **7**.

Sex-specific compounds that have intense antennal activity are considered likely pheromone components, as has been demonstrated with the aggregation pheromones in other coleopterans.[7,15] However, field tests are needed to finally define the behavioral function of this male-specific compound.

Experimental Section

General Experimental Procedures. GC was conducted on a Hewlett-Packard 6890 instrument equipped with a flame-

ionization detection. Samples were injected in splitless mode using 30 m EC-1 and EC-5 capillary columns (0.25 mm i.d., 0.25 μm film thickness, Alltech). Temperature programs were from 50 to 275 °C at 15 °C/min. Retention index of the male-specific compound was calculated relative to *n*-alkanes on a EC-1 column. GC−MS was performed using a Hewlett-Packard 5973 instrument interfaced to an HP 6890 GC. The spectra were acquired in electron impact (EI, 70 eV), positive (PCI, methane, and isobutane), and negative chemical ionization (NCI, methane) modes. The Wiley MS library,[16] with 275 821 spectra, was installed on the data system. HREIMS were recorded on a Micromass 70-VSE mass spectrometer. HPLC purification was carried out with a Waters 515 pump and Waters R401 differential refractometer detector equipped with a Si gel column (Econosphere silica, 5 μm particle size, 4.6 × 250 mm, Alltech). NMR spectra were obtained on a Bruker Avance 400 instrument (^{1}H and COSY at 400 MHz, ^{13}C and DEPT at 100 MHz).

Insect Material. The insects were field collected during late summer and early fall of 2000 from cereal leaf beetle infested oat fields at Yellowstone County, MT, and Park County, WY. The beetles were placed in cages containing oat seedlings and moist cardboard rolls for shelter and cooled from 15 to 4 °C over a 10 day period for winter storage in total darkness (Ruthann Berry, USDA/APHIS/PPQ, unpublished). Beetles were kept under these conditions for at least 4 months. After this period the beetles were removed from the cardboard rolls, and male and female beetles were placed in separate cages with oat seedlings as food source (room temperature, 14:10 h light:dark). Insects used in this study were kept at least one week at room temperature before commencing with volatiles collections.

Volatiles Collections. One- to three-day volatiles collections were made from individuals or groups of up to 10 male or female beetles feeding on oat seedlings. The beetles were placed into a horizontal glass tube (5 cm in diameter × 20 cm in length) containing oat seedlings in a small water vial. The tube had a 24/40 ground glass joint at both ends, into which thermometer adaptors were fitted; each of these contained a volatiles trap. The traps were made from 5 mm diameter glass tubing and contained a 5−8 mm plug of Super-Q porous polymer (80−100 mesh, Alltech). The Super-Q was held in place by fine stainless steel screen (which was fused into the trap wall) and glass wool. Emitted volatiles were trapped by placing a gentle vacuum on one of the traps so that air flowed through the tubes at about 100 mL/min. The other trap served to clean the incoming air. The volatiles were rinsed from the traps into vials with 300 μL of hexane, and host plant material was replaced as needed. The volatiles collectors were kept in an incubator at 27 °C with a relative humidity of about 50%. Light was provided by eight 40 W fluorescent tubes set about 0.5 m above and behind the apparatus. The daily light cycle was 14:10 h light:dark. All the collection glassware was silanized to reduce sample adsorption.

Electrophysiology. Collected volatiles of oat seedlings and oat seedling infested with insects were separated by capillary GC with the column effluent split between two detectors: the antenna of a cereal leaf beetle and the FID of the GC (GC-EAD). GC-EAD analyses were generally made using previously described methods and equipment.[15] GC-EAD connections were made by inserting a glass-pipet Ag/AgCl-grounding electrode into the back of an excised beetle head. A second glass-pipet Ag/AgCl-recording probe was placed in contact with the distal end of one antenna. Both pipets were filled with physiological saline. The simultaneously obtained GC and amplified EAD profiles were analyzed by Syntech GC-EAD computer software.

Microchemical Reactions. Hydrogenation of purified male-specific material was conducted at room temperature. Hydrogen was bubbled from a fine needle for about 5 min into 100 μl of ethanol, containing 10−100 ng of sample and a trace of platinum oxide (Adam's catalyst). Samples were analyzed by GC−MS. The hydrogenation product was reacted with $LiAlH_4$. The product was placed in 0.5 mL of ether in a conical vial together with ~10 μL of 1 M $LiAlH_4$ in ether for about 5 min. Excess $LiAlH_4$ was destroyed by dropwise addition of wet ether. The ether solution was washed with a similar volume of water, and the layers were separated. The organic layer was filtered (Pasteur pipet with glass wool plug) and dried over Na_2SO_4. Sample was analyzed by GC−MS.

THP Ether of Geraniol (2). A solution of geraniol (**1**) (10 g, 65 mmol, 98% pure, Aldrich) and dihydropyran (DHP) (8.4 g, 100 mmol) in dry methylene chloride (100 mL) containing pyridinium *p*-toluenesulfonate (PPTS) (1.6 g, 6.5 mmol) was stirred at room temperature.[10] The reaction was monitored by GC and was 98% complete after 4 h. The solution was diluted with ether, washed with half-saturated brine, and dried over Na_2SO_4. The solvent was removed by rotary evaporation, and after distillation (Kugelrohr, 0.3 Torr, 80 °C oven temperature), **2** was obtained as a colorless oil (15.2 g, purity 96% by GC): ^{13}C NMR (C_6D_6, 100 MHz) δ 139.1, 131.3 (s); 124.6, 122.0, 97.3 (d); 63.5, 61.4, 39.9, 31.0, 26.8, 26.0, 19.5 (t); 25.7, 17.6, 16.3 (q). The ^{1}H NMR and EIMS spectral data for **2** were in agreement with those reported.[17,18]

Geraniol THP Epoxide (3). A solution of **2** (7.55 g, 31.7 mmol) in dry methylene chloride (10 mL) was added dropwise to a solution of *m*-chloroperbenzoic acid (mCPBA) (8.20 g, 47.5 mmol) in methylene chloride (320 mL) containing 110 mL of 0.5 M $NaHCO_3$ and was stirred at room temperature.[11] The reaction was monitored by GC and was 99% complete after 5 h. The reaction mixture was separated into layers, and the organic layer was washed successively with 2% NaOH and water (2×) and dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation, and after distillation (Kugelrohr, 0.05 Torr, 80 °C oven temperature), **3** (7.57 g) was obtained as colorless oil (purity 62% by GC). A small amount of **3** was further purified by LC (SiO_2, 10% ether in hexane) for analytical purposes (purity 90% by GC): ^{13}C NMR (C_6D_6, 100 MHz) δ 138.5, 57.4 (s); 122.3, 97.5, 63.3 (d); 63.6, 61.5, 36.6, 31.0, 27.6, 25.9, 19.6 (t); 24.9, 18.8, 16.3 (q). The ^{1}H NMR and EIMS spectral data for **3** were in agreement with those reported.[17]

THP Ether of (*E*)-6-Hydroxy-4-methyl-4-hexenal (4). H_5IO_6 (3.6 g, 15.8 mmol) in dry ether (310 mL) was stirred for 1 h at room temperature until it was almost fully dissolved. The resulting solution was added dropwise over 20 min to **3** (3.80 g, 15.0 mmol) dissolved in 250 mL of dry ether and stirred at room temperature. The reaction was monitored by GC and was 100% complete after 30 min. The solution was washed successively with water and 10% $NaHCO_3$ and dried over anhydrous Na_2SO_4. The resulting crude **4** (purity 80% by GC) was used in the next step without further purification. A small amount of crude **4** was further purified by HPLC (25% ether in hexane) for analytical purposes (purity 91% by GC): ^{1}H NMR (C_6D_6, 400 MHz) δ 9.28 (1H, s), 5.42 (1H, tq, J = 5.3, J = 1.3), 4.69 (1H, t, J = 3.4), 4.33 (1H, dd, J = 12.0, J = 6.3), 4.05 (1H, dd, J = 12.0, J = 7.1), 3.88 (1H, m), 3.44 (1H, m), 2.03 (2H, t, $J \approx 7$), 1.94 (2H, t, $J \approx 7$), 1.90 (1H, m), 1.67 (2H, m), 1.43 (3H, s), 1.31 (3H, m); ^{13}C NMR (C_6D_6, 100 MHz) δ 137.4 (s); 200.0, 122.5, 97.6 (d); 63.5, 61.6, 41.8, 31.6, 31.0, 25.9, 19.6 (t); 16.3 (q); EIMS *m*/*z* (rel int) 197 (0.4), 168 (1), 111 (28), 101 (4), 93 (35), 85 (100), 81 (13), 67 (23), 55 (30), 41 (22).

1-THP Ether of (*E*)-3-Methyl-2-octen-1,6-diol (5). Et-MgBr (1.0 M solution in tetrahydrofuran, 17.5 mL, 17.5 mmol) was chilled over ice in an argon atmosphere. Crude **4** (~15 mmol) was diluted with 10 mL of dry ether and was added over 15 min. The mixture was stirred for an additional 30 min, monitored by GC (98% complete), and then chilled over ice. The reaction mixture was diluted with ether, and excess reagent was decomposed by adding dropwise saturated NH_4-Cl (20 mL). The layers were separated, and the organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed by rotary evaporation, and distillation (Kugelrohr, 0.05 Torr, 80 °C oven temperature) yielded **5** (2.4 g) as a colorless oil (purity 66% by GC). A small amount of **5** was further purified by HPLC (50% ether in hexane) for analytical purposes (purity 88% by GC): ^{1}H NMR (C_6D_6, 400 MHz) δ 5.66 (1H, tq, J = 5.3, J = 1.3), 4.78 (1H, t, J = 3.4), 4.47 (1H, dd, J = 12.0, J = 6.3), 4.17 (1H, m), 3.93 (1H, m), 3.51 (1H, m),

3.31 (1H, m), 2.17 (1H, m), 2.05 (1H, m), 1.86 (1H, m), 1.71 (2H, m), 1.66 (3H, s), 1.5−1.3 (7H, m), 0.91 (3H, t, $J = 7.4$); ^{13}C NMR (C_6D_6, 100 MHz) δ 139.6 (s); 121.9, 97.6, 72.5 (d); 63.7, 61.6, 36.2, 35.3, 31.1, 30.6, 25.9, 19.6 (t); 16.4, 10.1 (q); EIMS *m*/*z* (rel int) 211 (0.7), 158 (3), 141 (7), 129 (4), 125 (16), 123 (18), 111 (11), 101 (4), 93 (6), 85 (100), 81 (32), 67 (27), 57 (18), 41 (16).

THP Ether of (*E*)-8-Hydroxy-6-methyl-6-octen-3-one (6). A solution of pyridinium dichromate (PDC) (5.4 g, 14.4 mmol) and pyridinium trifluoroacetate (PTFA) (0.7 g, 3.8 mmol) in methylene chloride (40 mL) containing **5** (2.3 g, 9.6 mmol) was stirred at room temperature.[14] The reaction was monitored by GC and was 65% complete after 4 h. Additional amounts of PDC (5.4 g 14.4 mmol) and PTFA (0.7 g, 3.8 mmol) were added at this point, and the reaction mixture was stirred for an additional 6 h (100% complete). The reaction mixture was diluted with ether, filtered, and dried over Na_2SO_4. The solvent was removed by rotary evaporation. Traces of Cr salts were removed by LC (SiO_2, 15% ether in hexane), giving a colorless oil, **6** (1.24 g, purity 85% by GC), after evaporation of the solvent: ^{1}H NMR (C_6D_6, 400 MHz) δ 5.51 (1H, tq, $J =$ 5.3, $J = 1.3$), 4.75 (1H, t, $J = 3.4$), 4.42 (1H, dd, $J = 12.0$, $J =$ 6.3), 4.13 (1H, dd, $J = 12.0$, $J = 7.1$), 3.92 (1H, m), 3.50 (1H, m), 2.28 (2H, t, $J \sim 7$), 2.14 (2H, t, $J \sim 7$), 1.94 (2H, q, $J = 7.3$), 1.85 (1H, m), 1.71 (2H, m), 1.56 (3H, s), 1.50−1.26 (3H, m), 0.97 (3H, t, $J = 7.4$); ^{13}C NMR (C_6D_6, 100 MHz) δ 208.3, 138.3 (s); 122.0, 97.6 (d); 63.6, 61.6, 40.4, 35.6, 33.5, 31.1, 25.9, 19.6 (t); 16.5, 7.9 (q); EIMS *m*/*z* (rel int) 156 (9), 139 (23), 121 (9), 111 (3), 101 (2), 95 (3), 85 (100), 81 (11), 67 (21), 57 (68), 41 (12).

(*E*)-8-Hydroxy-6-methyl-6-octen-3-one (7). A solution of **6** (1.24 g, 5.2 mmol) in 10 mL of methanol containing pyridinium *p*-toluenesulfonate (PPTS) (130 mg, 0.5 mmol) was refluxed under argon atmosphere.[10] The reaction was monitored by GC and was 95% complete after 1.5 h. The methanol was removed by rotary evaporation (∼50 °C, 20 Torr). The residue was diluted with ether (10 mL), and the precipitate was filtered off by rinsing through a glass wool plug. The ether solution was washed with 2 mL of brine (2×) and dried over Na_2SO_4. The solvent was removed by rotary evaporation and yielded **7** as a colorless oil (420 mg, purity 88% by GC): ^{1}H NMR (C_6D_6, 400 MHz) δ 5.27 (1H, tq, $J = 6.6$, $J = 1.3$), 3.93 (2H, d, $J = 6.4$), 2.18 (2H, br t, $J \approx 8$), 2.04 (2H, br t, $J \approx 8$), 1.89 (2H, q, $J = 7.3$), 1.38 (3H, br s), 0.93 (3H, t, $J = 7.3$); ^{13}C NMR (C_6D_6, 100 MHz) δ 208.3 (s, C3), 137.1 (s, C6); 124.8 (d, C7); 59.2 (t, C8), 40.3, 35.5, 33.3 (t, C2, C4, C5); 16.2 (q, C6a), 7.9 (q, C1); EIMS *m*/*z* (rel int) 156 [M^+] (0.1), 138 [$M - H_2O$] (6), 123 (2), 109 (3), 97 (9), 84 (43), 81 (19), 79 (10), 72 (7), 67 (12), 57 (100), 43 (18), 41 (21); HREIMS *m*/*z* 138.1031 [$M - H_2O$] (calcd for $C_9H_{14}O$, 138.1044).

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References and Notes

(1) Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.
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