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SHORT AND STEREOSELECTIVE SYNTHESES OF PHEROMONE COMPONENTS OF APROAEREMA MODICELLA

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Abstract: Efficient syntheses of pheromone components of Aproaerema modicella starting from a common intermediate 7-octyn-1-ol is described.

The groundnut leafminer, Aproaerema modicella Deventer, is the most notorious insect pest of groundnuts in India and is also a serious pest of groundnuts and soyabeans throughout South and South-east Asia.[1] The larvae feed on the leaves and pupae by folding the leaves and damages the plant. It is difficult to control this pest by insecticidal application as they hide under the leaves by folding around themselves. The control of this kind of pests by pheromonal application would be the most suited method.

Pheromones isolated from the female groundnut leafminer consists of mixture of ten carbon acetates, including a terminal

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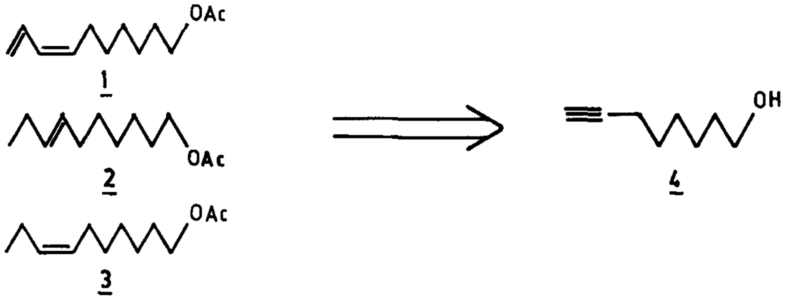
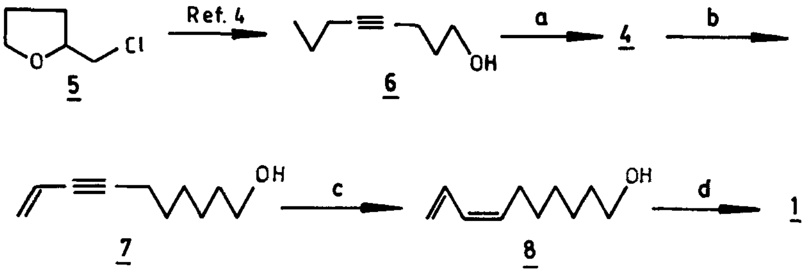
conjugated diene **1** and corresponding monoenes of E and Z configuration **2** and **3** in the ratio of 10:2:1.4. Conjugated terminal dienes are unusual pheromone components. The 12-carbon acetates[2] have been previously found as Lepidopterous sex pheromone components, but this is the first time that the 10-carbon acetate has been reported. As a part of our ongoing programme on the synthesis of insect sex pheromones of various indigenous crops,[3] herein, we give a complete account for the practical preparation of **1**,**2** and **3** from a common intermediate 7-octyn-1-ol **4**. (Scheme 1).

Our strategy is based on the in situ alkylation of 4-pentyn-1-ol generated from the opening of tetrahydrofurfuryl chloride in presence of $LiNH_2$/liq NH_3 with propyl bromide leading to disubstituted acetylenic alcohol[4] **6**, which on Zipper isomerization[5] gave the key intermediate **4** (Scheme 2). This on palladium mediated C-C bond formation with vinyl bromide in the presence of cuprous iodide and diethyl amine gave enyne **7**, which on semihydrogenation with P-2 Nickel[6] followed by acetylation gave conjugated terminal diene pheromone **1**.

For mono olefinic pheromones, **4** was protected as its tetrahydropyranyl ether **9** and alkylated with ethyl bromide using $LiNH_2$/Liq NH_3 and HMPA as co-solvent to furnish **10**. Removal of THP protection yielded **10**, which on stereospecific reduction of acetylene to trans-olefin **11** using Na/Liq NH_3 followed by acetylation gave **2**, whereas Lindlar reduction of corresponding acetate **12** produced the pheromone **3** (Scheme 3).



Scheme - 1

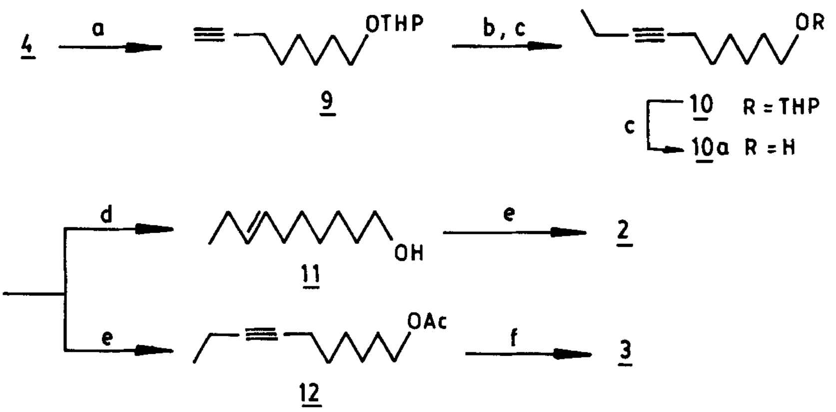


Reagents: a) $NaNH_2$, 1,3-diaminopropane ; b) $CH_2=CHBr$, $Pd(PPh_3)_4$, CuI, diethylamine, ether; c) P-2 Nickel, EtOH; d) Ac_2O, DMAP, pyridine

Scheme 2

EXPERIMENTAL

IR spectra were recorded on Perkin-Elmer 1310 spectrophotometer with NaCl optics. ^{1}H-NMR spectra were recorded on Varian Gemini-200 in $CDCl_3$ solvent containing TMS as internal standard and J values are given in Hz. Mass spectra were recorded on VG-70-70H double focussing mass spectrometer operating at 70 eV using direct inlet system.



Reagents: a) DHP, PTSA, CH_2Cl_2; b) $LiNH_2$, liq.NH_3, HMPA, EtBr; c) PTSA, MeOH; d) Na/liq.NH_3; e) Ac_2O, DMAP, pyridine; f) Pd-$CaCO_3$, H_2, EtOH

Scheme 3

7-Octyn-1-ol (4): A stirred suspension of sodium amide (1.4 g, 36 mmol) in dry 1,3-diaminopropane (25 ml) was heated to 80°C for 0.5 h. The reaction mixture was cooled to 0°C and treated with alcohol **6** (1.5 g, 12 mmol) and was heated for 4 h at 80°C, quenched with ice and extracted with ether. The ethereal layer was washed with water, 10% HCl, brine, dried (Na_2SO_4), concentrated and on purification by column chromatography afforded alkynol **4** (1.08 g, 72.1%). IR (neat): 3400, 3300, 2100 cm^{-1}. ^1H NMR: 1.2-1.6(8H,m), 1.8(1H,t), 2.2(2H,m), 3.6 (2H,t), m/z 126(M^+,4%); 93(62), 79(100), 67(87), 55(22), 41(60).

Dec-7-yn-9-en-1-ol (7): Diethylamine (50 ml), $Pd(PPh_3)_4$ (0.1 g), cuprous iodide (0.1 g) and terminal acetylenic alcohol **4**

(2.52 g, 20 mmol) are placed in the flask. The contents were warmed to 60°C and stirred for 1 h. Then vinyl bromide (40 mmol) alongwith 30 ml of dry ether was added in a portionwise manner at the same temperature keeping cold finger inside the flask for 2-3 h and stirred for 12 h at room temperature. During this period, ether was added for effective stirring. The suspension was filtered over sintered funnel and well rinsed with ether. The filtrate was concentrated and washed with aqueous ammonium chloride, water, brine, concentrated, dried (Na_2SO_4) and on purification by column chromatography afforded enyne **7** (2.28 g, 75%), IR (neat): 3400, 2210, 1600, 920 cm^{-1}, ^1H NMR: 1.2-1.7 (8H,m), 2.3 (2H,t), 3.6 (2H,t), 5.3-5.6 (3H,m), m/z 153(M^++1,37%), 135(97), 117 (85), 80(89), 67(59), 59(98), 43(100).

7Z-,9-Decadiene-1-ol (8): To a freshly prepared suspension of P-2 nickel [(prepared from nickel acetate (0.445 g, 0.0017 mol) and 1M ethanolic borohydride solution (1.78 ml)] in ethanol (15 ml) was added ethylene diamine (0.32 g, 5 mmol) followed by enyne **7** (0.3 g, 2 mmol) in ethanol (3 ml) and stirred under hydrogen till the required amount of hydrogen gas was absorbed. Then the reaction mixture was filtered over charcoal bed, solvent was removed, residue was taken in ethyl acetate, washed with water, brine, dried (Na_2SO_4), concentrated and on purification by column chromatography afforded diene **8** (0.22 g,71%). IR (neat): 3340, 2800, 2210, 1640, 920; ^1H NMR: 1.1-1.7 (8H,m), 2.1-2.3 (2H,m), 3.5 (2H,t), 4.9-6.0 (4H,m), 6.4-6.6 (1H,dt), m/z 154(M^+,21%), 91(25), 79(62), 67(100), 55(64).

7Z,9-Decadienyl-1-acetate (1): To a solution of diene alcohol **8** (0.77 g, 5 mmol) in 15 ml of dry pyridine, catalytic amount of DMAP was added. The reaction mixture was cooled to 0°C, acetic anhydride (5 ml) was added and stirred for 8 h at room temperature. The reaction mixture was quenched with ice and extracted with ethyl acetate, washed with 10% HCl, sodium bicarbonate solution, water, brine, dried (Na_2SO_4), concentrated and on column chromatography afforded pheromone **1** (0.88 g, 90%). IR (neat): 1740, 1640, 920; ^1H NMR: 1.1-1.7 (8H,m), 2.0 (3H,s), 2.1-2.2 (2H, m), 4.0 (2H,t), 4.9-6.0 (4H,m), 6.6 (1H,dt); m/z 196 (M^+,21%), 136((M^+-60,27), 79 (60), 67(93), 54(37), 43(100). Anal. calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C,73.40; H,10.22.

1-[(Tetrahydro-2H-pyran-2-yl)oxy]-7-octyne (9): To a solution of alcohol **4** (1.26 g, 10 mmol) at 0°C taken in dry DCM, catalytic amount of PTSA was added. To this, dihydropyran (1.15 g, 12 mmol) was added and stirred at room temperature for 8 h. The reaction mixture was quenched with sodium bicarbonate, then washed with water, brine, dried (Na_2SO_4), concentrated and on purification by column chromatography afforded alcohol THP ether **9** (1.8 g, 85%). IR (neat): 3270, 2800, 2100, 1240, 1150, 1120, 1070, 1025; ^1H NMR: 1.2-1.7 (16H,m), 1.8 (1H,t), 2.0-2.2 (2H,m), 3.3-3.9 (4H,m), 4.5 (1H,bs); m/z 168(25%), 125(4), 85(100), 67(23), 55(35), 41(52).

1-[(Tetrahydro-2H-pyran-2-yl)oxy]-7-decyne (10): To a freshly prepared lithium amide [prepared from lithium (0.25 g, 36 g atm) in liq NH_3 (100 ml)], alcohol THP ether **9** (5 g, 24 mmol) was added, after 0.5 h, 5-10 ml of HMPA was added as co-solvent, then stirred for 2 h at -33°C, followed by addition of ethyl bromide (5.2 g, 48 mmol in 10 ml of THF) was added and reaction mixture was stirred for 6 h at -33°C. Ammonia was allowed to evaporate, quenched with aqueous ammonium chloride and extracted with ether. The combined ethereal layers were washed with water, brine, dried (Na_2SO_4), concentrated and on purification by column chromatography afforded alkylated THP ether **10** (4 g, 70%). IR (neat): 2010, 1150, 1120, 1070, 1025; ^1H NMR: 1.1 (3H,t), 1.2-1.7 (16H,m), 2.2 (4H,m), 3.3-3.9 (4H,m), 4.5 (1H,bs); m/z 95(13%), 85(100), 67(16), 55(22), 41(34).

7-Decyn-1-ol (10a): To a solution of alkylated THP ether **10** (2.38 g,10 mmol) in aq methanol (20 ml), catalytic amount of PTSA was added and stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the residue was taken in ethyl acetate, quenched with sodium bicarbonate and washed with water, brine, dried (Na_2SO_4), concentrated and on purification by column chromatography afforded alcohol **10a** (1.38 g,90%). IR (neat): 3340, 2080 cm^{-1}; ^1H NMR: 1.1(3H,t), 1.2-1.7 (8H,m), 2.1-2.2 (4H,m), 3.6 (2H,t); m/z 154(M^+,4%), 105(29), 91(52), 79(87), 67(100), 55(33).

7E-Decen-1-ol (11): Alkynol **10a** (1.84 g,12 mmol) was taken in a freshly distilled liq NH_3 and stirred vigorously. To this solution sodium (1.1 g, 48 g atm) was added in small portions. After 2 h excess sodium was decomposed by adding ammonium chloride. Dilute aqueous ammonia was then carefully added and the solution was extracted with ether and washed with water, brine, dried (Na_2SO_4), concentrated and on purification by column chromatography afforded trans-alcohol **11** (1.46 g,78%). IR: (neat): 3340, 970; ^{1}H NMR: 0.9 (3H,t), 1.2-1.7 (8H,m), 2 (4H,m), 3.6 (2H,t), 5.4 (2H,m); m/z 156 (M^+,6%), 91(50), 79(90), 67(100), 55(30).

7E-Decen-1-acetate (2): Alkenol **11** (1.56 g,10 mmol) was acetylated in the same way as described for compound **1** to give pheromone **2** (1.78 g,90%). IR (neat): 1750, 970 cm^{-1}; ^{1}H NMR: 0.9 (3H,t,J 7.5), 1.1-1.6 (8H,m), 1.9 (4H,m), 2.05 (3H,s), 4.0 (2H,t, J=6.7), 5.3-5.4 (2H,m); m/z 198(M^+,16), 138 (M^+-60,46), 95(47), 82(80), 67(86), 43(100). Anal. calcd. for $C_{12}H_{22}O_2$: C,72.68, H,11.18. Found: C,72.66; H,11.14.

7-Decyn acetate (12): Alkynol **10a** (1.54 g, 10 mmol) was acetylated in the same way as described for compound **1** to give acetate **12** (1.76 g, 88.8%). IR (neat): 2080, 1750 cm^{-1}; ^{1}H NMR: 1.1 (3H,t), 1.2-1.8 (8H,m), 2 (3H,s), 2.1-2.2 (4H,m), 4 (2H,t); m/z 196(M^+,4%), 93(35), 79(66), 67(46), 55(19), 43 (100).

7Z-Decen-1-acetate (3): Acetate **12** (0.98 g,5 mmol) was partially hydrogenated at atmospheric pressure over Lindlar catalyst in absolute ethanol (15 ml) containing two drops of quinoline till the required amount of hydrogen was absorbed. Catalyst was filtered and the filtrate was washed with 10% HCl, water, brine, dried (Na_2SO_4), concentrated and on purification by column chromatography afforded pheromone **3** (0.84 g,85%). IR (neat): 1750, 740 cm^{-1}; ^{1}H NMR: 0.9 (3H,t), 1.2-1.7 (8H,m), 1.8-2.1 (7H, m), 4 (2H,t,J 6.6), 5.2-5.4 (2H,m); m/z 198(M^{+},2%), 138(M^{+}-60,79), 95(85), 82(91), 67 (100). Anal. calcd. for $C_{12}H_{22}O_{2}$: C, 72.68; H,11.18. Found: C,72.66; H,11.16.

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