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Synthesis of 6*Z*,8*E*-heneicosadien-11-one, a sex pheromone of the painted apple moth, *Teia anartoides*

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Abstract—6*Z*,8*E*-Heneicosadien-11-one, a sex pheromone of the painted apple moth, *Teia anartoides* has been prepared in seven steps from 1,2-epoxydodecane in an overall yield of 25%. © 2002 Elsevier Science Ltd. All rights reserved.

The painted apple moth, *Teia anartoides* (Lepidoptera: Lymantriidae), a native of Australia's southeastern mainland and Tasmania,[1] has been identified as a recent arrival to New Zealand where it is considered a pest of significant economic importance.[2] As part of an ongoing eradication program,[3] 6*Z*,8*E*-heneicosadien-11-one **1** was required for the formulation of a synthetic pheromone blend to monitor the distribution of the painted apple moth. Dienone **1** has been reported previously as a synergistic sex pheromone of the Douglas-fir tussock moth,[4] however, its synthesis, employing a Wittig strategy, yielded a mixture of isomeric polyenes requiring extensive purification by silver nitrate mediated preparative chromatography.[4] To prepare sufficient quantities of isomerically pure dienone **1** for insect lures, an alternative more stereoselective synthesis was investigated (Fig. 1).

Lithium acetylide–EDA complex was reacted with 1,2-epoxydodecane **2** in DMSO at room temperature[5] and silylation of the resulting secondary alcohol, under standard conditions,[6] gave the TBS protected tetradecynol **3** in 83% yield over the two steps. *E*-Vinyl iodide **4** was obtained as a single stereoisomer in good yield by the hydrozirconation–iodination[7] of acetylene **3** with Schwartz's reagent[8] and freshly sublimed iodine.

Sonogashira coupling[9] of iodide **4** with 1-heptyne proceeded smoothly and enyne **5** was isolated in quantitative yield after chromatography on silica gel. Initial attempts to reduce selectively the conjugated enyne **5** to the *E*,*Z*-diene **6** under a variety of conditions, including Lindlar's catalyst[10] and disiamylborane,[11] proved unsuccessful. Formation of the protected-*E*,*Z*-dienol **6** was however achieved in good yield by the partial

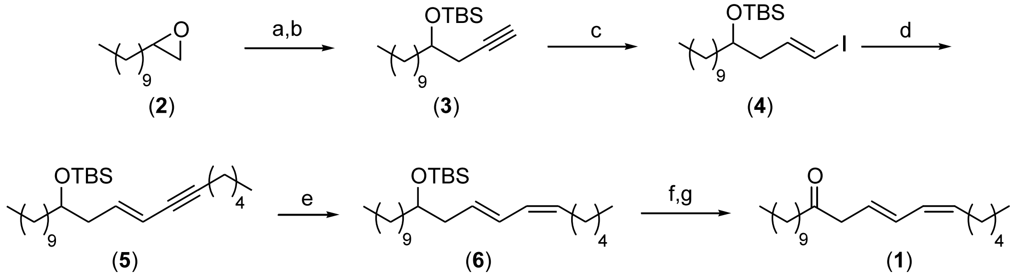

Figure 1. *Synthesis of 6Z,8E-heneicosadien-11-one* ***1****; reagents and conditions.* (a) LiC≡CH:$H_2NCH_2CH_2NH_2$, DMSO, rt, 86%; (b) TBDMSCl, imidazole, DMF, 0°C, 97%; (c) (i) Cp_2ZrHCl, PhH, rt, dark, 48 h, (ii) I_2, 65%; (d) 1-heptyne, $PdCl_2(CH_3CN)_2$, CuI, piperidine, rt, quant.; (e) (i) $Ni(OAc)_2$:$4H_2O$, $NaBH_4$, EtOH, 0°C, (ii) $H_2NCH_2CH_2NH_2$, **5**, H_2, rt, 69%; (f) TBAF, CH_2Cl_2, rt, 78%; (g) PCC, K_2CO_3, rt, CH_2Cl_2, 87%.

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reduction of **5** in the presence of catalytic P2-Ni under a hydrogen atmosphere.[12] Observed coupling constants of 15.0 and 11.2 Hz in the ^{1}H NMR spectrum[13] and comparison with the spectra of other dienes[14] confirmed the stereochemistry of the protected dienol **6** as 6*Z*,8*E*. Fluoride mediated deprotection of the silyl ether and PCC oxidation of the secondary alcohol concluded the synthesis of dienone **1**. The synthetic material[15] was identical by GC–MS to the natural material isolated from the female painted apple moth.[16]

In conclusion, 6*Z*,8*E*-heneicosadien-11-one **1** has been prepared stereoselectively in seven steps from readily available starting materials in an overall yield of 25%. Dienone **1** is currently under evaluation as a synthetic sex pheromone for the painted apple moth and its use to control this pest will be reported in due course.

Acknowledgements

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13. 11-*tert*-Butyldimethylsiloxyheneicosa-(*Z*)6,(*E*)8-diene **6** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.32 (1H, dd, $J=15.0$, 11.2 Hz, H8), 5.96 (1H, dd, $J=11.2$, 11.2 Hz, H7), 5.65 (1H, dt, $J=15.0$, 7.5 Hz, H9), 5.33 (1H, dt, $J=11.2$, 7.6 Hz, H6), 3.69 (1H, quint., $J=5.7$ Hz, H11), 2.29–2.23 (2H, m, H10), 2.21–2.14 (2H, m, H5), 1.45–1.28 (24H, m, H2-H4 and H12-H20), 0.93–0.88 (15H, m, H1, H21, and -$SiC(CH_3)_3$), 0.06 (3H, s, -$SiCH_3$), 0.05 (3H, s, -$SiCH_3$) ppm; ^{13}C NMR ($CDCl_3$, 400 MHz) δ 130.7 (C9), 130.4 (C6), 128.6 (C7), 127.8 (C8), 72.3 (C11), 41.0 (C10), 37.1, 32.0, 31.5, 29.8, 29.7, 29.7, 29.5, 29.4, 27.7, 25.9, 25.4, 22.7, 22.6, 18.1, 14.1, 14.1, −4.4, −4.5 ppm.
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15. Found M^+ 306.2929; $C_{21}H_{38}O$ requires 306.2923; ν_{max} (thin film) 2956, 2926, 2855, 1717, 1466, 1377, 1365, 984 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.38 (1H, ddq, $J=15.2$, 11.2, 1.2 Hz, H8), 5.98 (1H, dd, $J=11.2$, 11.2 Hz, H7), 5.73 (1H, dt, $J=15.2$, 7.4 Hz, H9), 5.40 (1H, dt, $J=11.2$, 7.7 Hz, H6), 3.20 (2H, d, $J=7.4$ Hz, H10), 2.43 (2H, t, $J=7.5$ Hz, H12), 2.18–2.12 (2H, m, H5), 1.64–1.10 (22H, m, H2-H4, H13-H20), 0.90–0.86 (6H, m, H1 and H21) ppm; ^{13}C NMR ($CDCl_3$) δ 209.2 (C11), 132.2 (C6), 129.4 (C8), 127.8 (C7), 125.0 (C9), 46.9 (C10), 42.4 (C12), 31.8, 31.4, 29.7, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 23.7, 22.7, 22.5 (C2-C5, C13-C20), 14.1, 14.0 (C21 and C1) ppm; MS m/z (rel. int.%) 306 (M^+ 6), 221(4), 170(9), 169(100), 109(10), 95(32), 85(46), 81(20), 71(44), 67(30), 57(69), 43(65).
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