# STEREOSELECTIVE SYNTHESIS OF (*Z*)-7-OCTADECENYL ISOVALERATE, A SEX PHEROMONE OF *Euproctis similis xanthocampa*

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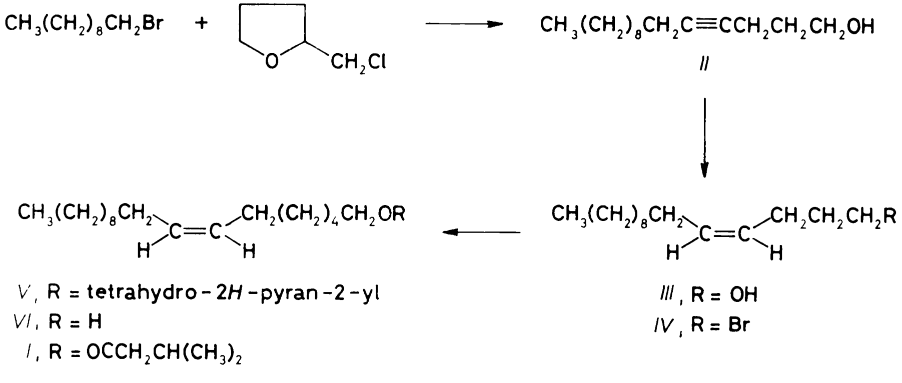
A simple stereoselective synthesis of (*Z*)-7-octadecen-1-yl isovalerate (*I*), a sex pheromone of *Euproctis similis xanthocampa* has been achieved through an unambiguous route. The isovalerate type of sex pheromones was discovered in *Limantxiidase* for the first time.

(Z)-7-Octadecen-1-yl isovalerate has been identified[1] from the sex pheromone gland washings of *Euproctis similis xanthocampa* (*Limantxiidae, Lepidoptera*), as determined by GC-MS analysis, microozonolysis and methyl transesterification. The synthetic (Z)-7-octadecenyl isovalerate (*I*) was as active as the one obtained from virgin female moths both in field test or on EAG responses. We report herein a simple stereoselective synthesis of *I* (Scheme 1).



SCHEME 1

Pentadec-4-yn-1-ol (*II*) was obtained through the reaction of 1-bromodecane[2] with the dianion of 4-pentyn-1-ol prepared in situ from tetrahydrofurfuryl chloride[3,4] and lithium amide in liquid ammonia. Compound *II* was partially hydrogenated using Lindlar's catalyst[5] in hexane quantitatively to yield alcohol *III* which on subsequent reaction with phosphorous tribromide[6] and pyridine in dry ether gave bromide *IV*. Dilithium tetrachlorocuprate catalyzed[7] coupling reaction of *IV* with 3-bromo-1-(2-tetrahydropyranyloxy)propane in tetrahydrofuran at −10°C afforded *V*. Deprotection[8] of the coupled product *V* yielded the alcohol *VI* which on esterification with isovaleryl chloride and pyridine[9] in dichloromethane furnished the title compound *I*.

## EXPERIMENTAL

Boiling points are uncorrected. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer (wavenumber in $cm^{-1}$) and $^1H$ NMR spectra in $CCl_4$ on a Varian EM-390 (90 MHz) spectrometer using tetramethylsilane as an internal standard. Chemical shifts are given in ppm ($\delta$ scale). Silica gel (Acme, 60–80 mesh) was used for column chromatography. Unless otherwise stated, all organic extracts were dried over anhydrous sodium sulphate.

### Pentadec-4-yn-1-ol (*II*)

To the freshly distilled liquid ammonia (500 ml) was added lithium (2·1 g, 300 mmol) in presence of catalytic amount of iron(III) nitrate to form a suspension of lithium amide. Tetrahydrofurfuryl chloride (12·05 g, 100 mmol) was then added during 10 min to the above suspension of lithium amide. The reaction mixture was stirred for 2 h, followed by slow addition of a solution of 1-decyl bromide (22·1 g, 100 mmol) in dry tetrahydrofuran (30 ml) and stirring for an additional 3 h. Ammonia was allowed to evaporate and the reaction quenched with saturated ammonium chloride solution. It was extracted with ether, washed with water, brine and dried. Solvent removal followed by distillation of the residue gave *II* 15·68 g, (70%), b.p. 126–128°C/133 Pa. IR spectrum (neat): 3 400 (OH), 2 150 ($C{\equiv}C$). $^1H$ NMR spectrum: 3·8 s, 1 H (OH); 3·5 t, 2 H ($CH_2OH$); 2·0–2·1 m, 4 H (2 × $CH_2{-}C{\equiv}C$); 1·2–1·6 m, 18 H (9 × $CH_2$); 0·9 t, 3 H ($CH_3$).

### (*Z*)-4-Pentadecen-1-ol (*III*)

The alcohol *II* (8 g, 35·7 mmol) was partially hydrogenated over Lindlar's catalyst (300 mg) in dry hexane (25 ml) containing one drop of quinoline. Hydrogen pressure (280 kPa) was applied and stirred. When one equivalent of hydrogen was taken up, the catalyst was filtered off, the solution washed successively with dilute acetic acid, water and dried. Evaporation of the solvent and purification by column chromatography furnished the alcohol *III* 7·34 g (91%), b.p. 124–126°C/106 Pa. IR spectrum (neat): 3 400, 1 640, 725. $^1H$ NMR spectrum: 5·2–5·4 m, 2 H (2 × $H{-}C{=}C$); 3·7 s, 1 H (OH); 3·5 t, 2 H ($CH_2OH$); 2·0–2·1 m, 4 H ($CH_2{-}CH{=}C$); 1·2–1·6 m, 18 H (9 × $CH_2$), 0·9 t, 3 H ($CH_3$).

### (*Z*)-1-Bromo-4-pentadecene (*IV*)

To a solution of alcohol *III* (4·0 g, 18 mmol) in ether (150 ml) containing pyridine (3–4 drops), was added phosphorus tribromide (0·847 ml, 8·9 mmol) dropwise at 0°C and allowed the reaction mixture to stand overnight. After refluxing for 2 h the reaction mixture was cooled, poured into iced water, extracted with ether, washed with 5% sodium hydrogen carbonate solution, brine and dried. Evaporation of the solvent furnished *IV* 3·83 g, (75%). IR spectrum showed absence of absorption in the hydroxyl region. $^1H$ NMR spectrum gave signal 3·5 t, 2 H ($CH_2Br$).

### (*Z*)-1-(2-Tetrahydro-2*H*-pyranyloxyl)-7-octadecene (*V*)

To the Grignard reagent prepared from 3-bromo-1-(2-tetrahydropyranyloxy)propane (2·67 g, 12 mmol) and magnesium (0·288 g, 12 mmol) in tetrahydrofuran (10 ml) was added bromide *IV* (2·89 g, 10 mmol) in tetrahydrofuran at −10°C under nitrogen atmosphere. The contents were stirred for 45 min followed by addition of 0·1M solution of dilithium tetrachlorocuprate in tetrahydrofuran (2 ml) and the reaction mixture stirred at 0°C for another 3 h and left to stand overnight. The reaction mixture was decomposed with saturated ammonium chloride solution, extracted with ether, washed with brine and dried. Evaporation of the solvents and purification by column chromatography gave *V* 1·93 g, (55%). IR spectrum (neat): 1 640, 920, 875, 800, 725. $^1$H NMR spectrum: 5·2−5·5 m, 2 H (2 × H—C=C); 4·6 s, 1 H (H-2 of tetrahydropyranyloxy group); 3·3−3·7 m, 4 H (2 × $OCH_2$); 1·9−2·1 m, 4 H ($CH_2$—CH=C); 1·1−1·6 m, 30 H (15 × $CH_2$); 0·9 t, 3 H ($CH_3$).

### (*Z*)-7-Octadecen-1-ol (*VI*)

A solution of *V* (1·93 g, 6 mmol) in methanol (30 ml) containing *p*-toluenesulfonic acid (200 mg, 1 mmol) was stirred at room temperature for 6 h. Methanol was evaporated, the residue was treated with ether, ethereal solution was washed with sodium bicarbonate solution, water, brine and dried. Evaporation of the solvent yielded alcohol *VI* as the viscous oil. Yield 1·17 g, (80%). IR spectrum (neat): 3 400, 1 640, 725. $^1$H NMR spectrum: 5·3−5·6 m, 2 H (2 × H—C=C); 3·9 s, 1 H (OH); 3·6 t, 2 H ($CH_2OH$); 1·9−2·2 m, 4 H ($CH_2$—CH=C); 1·1−1·6 m, 24 H (12 × $CH_2$); 0·9 t, 3 H ($CH_3$).

### (*Z*)-7-Octadecen-1-yl Isovalerate (*I*)

A solution of compound *VI* (1·17 g, 4 mmol), isovaleryl chloride (0·64 ml, 5 mmol) and pyridine (0·42 ml, 5 mmol) in dichloromethane (10 ml) was stirred overnight at room temperature. It was then washed with 2M-HCl, 4% NaOH, brine, dried and evaporated to yield 1·48 g, (96%) of liquid ester *I*. IR spectrum (neat): 1 750, 1 640, 725. $^1$H NMR spectrum: 5·2−5·5 m, 2 H (2 × H—C=C); 3·3−3·6 t, 2 H ($OCH_2$); 2·0−2·4 m, 6 H; 1·1−1·5 m, 25 H (12 × $CH_2$ and CH); 0·8−1·0 m, 9 H (3 × $CH_3$). For $C_{23}H_{44}O_2$ (352·6) calculated: 78·34% C, 12·58% H; found: 78·38% C, 12·49% H.

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