

Facile Synthesis of (Z)-9-Hexadecen-1-ol and its Acetate

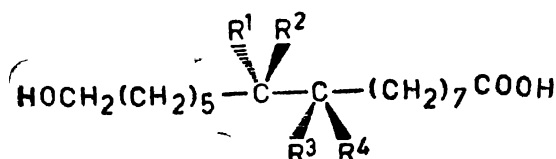
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The sex pheromones of certain noctuid moths contain (Z)-9-hexadecen-1-ol (7) and its acetate (8) as their components. Both the compounds are present in the sex pheromone of *Heliothis subflexa* (Gn.)¹ while the latter is present in those of *Mamestra brassicae* L.², *Pseudaletia unipuncta* and *Naranga aeneascens* M.³ These compounds can be synthesised from aleuritic acid, 9,10,16-trihydroxyhexadecanoic acid (1). Aleuritic acid can easily be obtained by alkaline hydrolysis of shellac⁴ which is produced in large quantities in India.

Chattopadhyay *et al.*⁵ reported synthesis of (Z)-9-hexadecen-1-yl acetate (8) from *threo* aleuritic acid which involved conversion of *E* to *Z* configuration through acetylenic route. *threo*-Aleuritic acid (1a) can easily be converted into its *erythro*-isomer (1b; 90%) which is a better candidate compound for the synthesis of the *Z*-isomer. Synthesis of compounds 7 and 8, mentioned above through *erythro*-aleuritic acid is reported here. *threo*-Aleuritic acid (1a) was converted into its *erythro*-isomer⁶ (1b) and then treated with phosphonium iodide to obtain 16-hydroxy-(Z)-9-hexadecenoic acid (2). Its tosyl derivative (3) was then prepared by treatment with toluene sulphonyl chloride in dry pyridine. This on treatment with sodium iodide in dry acetone yielded the iodo-derivative (4) which on reduction with NaBH₄/DMF gave (Z)-9-hexadecenoic acid (5). Its alcohol (7) was prepared by esterification followed by LAH reduction. Treatment of the aforesaid alcohol with acetic anhydride in pyridine yielded (Z)-9-hexadecen-1-yl acetate (8).



1a; R¹=R³=H, R²=R⁴=OH
1b; R¹=R⁴=H, R²=R³=OH

R¹-CH₂(CH₂)₅CH=CH(CH₂)₇COOR²

2; R¹=OH, R²=H
3; R¹=OTs, R²=H
4; R¹=I, R²=H
5; R¹=R²=H
6; R¹=H, R²=Me

CH₂(CH₂)₅CH=CH(CH₂)₇CH₂OR

7; R=H
8; R=COMe

Experimental

Boiling points reported are uncorrected. Ir and nmr spectra were recorded respectively on a Perkin-Elmer 237 spectrophotometer and a Perkin-Elmer R-32 instrument (90 MHz) using TMS as an internal standard. The compounds were routinely checked for their purity by tlc.

erythro-Aleuritic acid (1b): The *threo*-aleuritic acid (1a) was converted into its *erythro* form following reported procedure⁶.

16-Hydroxy-(Z)-9-hexadecenoic acid (2): *erythro* Aleuritic acid (1b; 1.6 g) in acetic acid (15 ml) was treated with phosphonium iodide (1.7 g)⁷ to obtain an oil which was purified by a column of neutral alumina. Elution of this compound with 25% ethyl acetate in benzene gave pure 2 (0.56 g); ν_{max} 3 250, 1 700 and 752 cm⁻¹ (CH=CH); ¹³C nmr δ (CDCl₃) 179.30 (C=O of carbonyl C-1), 130.3 and 130.5 (two *cis*-olefinic carbons at C-9 and C-10 respectively), 75.31 (CH₂OH at C-16), 58.5 and 57.5 (C-8 and C-11), 34.08 and 32.55 (C-2 and C-15) and 31–27, 25.39, 24.43 (methylene carbons).

16-Tosyloxy-(Z)-9-hexadecenoic acid (3): Toluene sulphonyl chloride (0.5 g) was slowly added to the above unsaturated acid (2; 0.5 g) in dry pyridine (25 ml) and kept at –5° for 15 h⁸. On usual work up, 3 was obtained as viscous liquid (0.51 g) which was purified by column chromatography; ν_{max} no hydroxyl absorption, 1 600, 1 465, 1 440 and 750 cm⁻¹; pmr δ (CDCl₃) 4.02 (t, CH₂OTS) and 5.27 (m, CH=CH).

16-Iodo-(Z)-9-hexadecenoic acid (4): 3 (0.35 g) was converted into its liquid iodo compound (4; 0.30 g) by refluxing with sodium iodide (0.35 g) in dry acetone (15 ml) for 16 h⁸; ν_{max} 1 700 and 752 cm⁻¹; pmr δ (CDCl₃) 3.12 (t, CH₂I) and 5.26 (m, CH=CH).

(Z)-9-Hexadecenoic acid (5): 4 (0.30 g) was reduced with sodium borohydride (0.18 g) in dimethyl formamide (5 ml) at 80° for 1 h and processed to yield 5 (0.26 g) which was purified by distillation at 162°/0.6 mm (lit.⁹ b.p. 162°/0.6 mm) (Found: C, 75.53; H, 11.72. C₁₆H₃₀O₂ calcd. for: C, 75.60; H, 11.81%); ν_{max} 1 705 and 752 cm⁻¹; pmr δ (CCl₄) 5.26 (2H, t, CH=CH).

Methyl (Z)-9-hexadecenoate (6): 5 (0.2 g) was esterified with methanol containing concentrated H₂SO₄ for 6 h on a steam-bath, and the product on usual work up yielded 6 (0.19 g); ν_{max} 1 740 and 751 cm⁻¹.

(Z)-9-Hexadecen-1-ol (7): The ester (6; 0.18 g) was reduced with lithium aluminium hydride (0.06 g) in dry tetrahydrofuran (5 ml) at room temperature for 24 h and processed to yield the product which was purified by distillation (0.14 g), m.p. 128–32°/0.5 mm; pmr δ (CDCl₃) 0.87 (3H, t, CH₂CH₃), 1.3 (20H, bs, 10 × CH₂), 1.9–2.1 (4H, m, CH₂CH=CH-CH₂), 2.45 (1H, bs, D₂O exchangeable), 3.63 (2H, t, CH₂OH) and 5.2–5.4 (2H, m, CH=CH).

(Z)-9-Hexadecen-1-yl acetate (8): Acetic anhydride (2 ml) was added to a solution of the alcohol (7; 0.12-g) in pyridine (2 ml) and the mixture was stirred for 1 h and then kept at room temperature for 24 h. On work up, the product was obtained as an oil (0.1 g) which was purified by distillation, b.p. 129–32°/0.15 mm (lit.⁵ 128–32°/0.15 mm) (Found: C, 76.52; H, 12.20. C₁₈H₃₄O₂ calcd. for: C, 76.70; H, 12.05%); ν_{\max} 2940, 2865, 1740, 1450, 1370, 1235, 1040 and 730 cm⁻¹; pmr δ (CDCl₃) 0.92 (3H, t, CH₂CH₃), 1.32 (20H, bs, 10 × CH₂), 2.0 (7H, m, CH₂CH=CHCH₂ and overlapped s, OCOCH₃), 4.06 (2H, t, CH₂OCOCH₃) and 5.40 (2H, m, CH=CH).

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