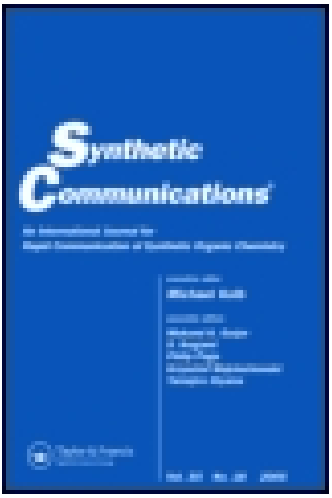

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Practical Syntheses of Some Insect Sex Pheromones, 10- and 12-Alken-1-ol Acetates

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PRACTICAL SYNTHESES OF SOME INSECT SEX PHEROMONES, 10- AND 12-ALKEN-1-OL ACETATES

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ABSTRACT Some insect sex pheromones 10-dodecen-1-ol acetates 5a(Z/E) and 12-tetradecen-1-ol acetates 5b(Z/E) have been synthesized from cis-13-docosenoic acid 1a and cis-15-tetracosenoic acid 1b via the isomerization of key intermediates 11-dodecen-1-ol acetate 4a and 13-tetradodecen-1-ol acetate 4b.

The sex pheromones of Lepidoptera insects are usually unsaturated straight-chain aliphatic alcohol acetates[1], having disubstituted double bonds. 10-dodecen-1-ol acetates 5a (Z/E) were identified as sex pheromones of some insects, such as Hedya atropunctana[2] and Laspeyresia nigricana[3]. For the synthesis of 5a(Z/E), few papers were reported[4],[5]. In addition, the key intermediate 4a is also a sex pheromone of a few insects, such as Homona magnanima[6]. Its synthetic methods previously reported are mainly from 1,12-dodecanediol as a starting material[7],[8]. 12-tetradecen-1-ol acetates 5b(Z/E) were identified as the sex pheromones of Ostrinia furnacalis Guenee (Asian Corn Borer)[9]. We previously reported[10] the synthetic methods of the pheromones 5b(Z/E).

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$$\underset{\text{1a,b}\ \ n=11,13}{CH_3(CH_2)_7CH{=}CH(CH_2)_nCOOH} \xrightarrow{\text{i,ii}} \underset{\text{2a,b}}{HO(CH_2)_{n+1}COOH}$$

$$\xrightarrow{\text{iii}} \underset{\text{3a,b}}{AcO(CH_2)_{n+1}COOH} \xrightarrow{\text{iv}} \underset{\text{4a,b}}{AcO(CH_2)_{n-1}CH{=}CH_2}$$

$$\xrightarrow{\text{v}} \underset{\text{5a,b(Z/E)}}{AcO(CH_2)_{n-2}CH{=}CHCH_3}$$

(i) O_3, C_2H_5OH-n-hexane, (ii) KBH_4, NaOH, H_2O, (iii) acetic anhydride, pyridine, (iv) $Pb(AcO)_4$, $Cu(AcO)_2$, pyridine, (v) $CoCl_2$, Ph_3P, $NaBH_4$.

Scheme

In this paper, a practical approach for the synthesis of 5a (Z/E) and 5b(Z/E) respectively from cis-13-docosenoic acid 1a and cis-15-tetracosenoic acid 1b is described(outlined in scheme). The key step in these syntheses is an isomerization of 4a and 4b to 5a(Z/E) and 5b(Z/E). Satyanarayana[11] reported the isomerization of terminal olefins by a $CoCl_2$ /Ph_3P /$NaBH_4$ system. According to their method, we completed the synthesis of 5a(Z/E) and 5b(Z/E) with a satisfactory yield of 70-80 %, the Z and E ratios of 5a and 5b have been analysed by GC.

Experimental

All melting and boiling points were uncorrected. IR spectra were recorded on a Shimadzu 450S infrared spectrophotometer. ^1H NMR spectra were measured with FX-90 spectrometer (90 MHz) using TMS as an internal standard and $CDCl_3$ as a solvent. Mass spectra were measured on a GC/MS QP1000 spectrometer. GC measurment was made on a Shimadzu GC-9A(Finnigan) instrument(30 m ×0.25 mm glass capillary column, carrier gas, N_2, 1.0 ml/min, column tempreture, 200℃). Column Chromatography silica gel 200-300 mesh (Tsing Dao Oceanography Chemical Factory).

13-Hydroxytridecanoic acid 2a and 13-acetoxytridecanoic acid 3a were synthesized according to Lit.[10].

Cis-15-tetracosenoic acid 1b was prepared as described in Lit.[12].

15-Hydroxypentadecanoic acid 2b:

According to Lit.[10], 30 g (80 mmol) of 1b was converted into 15.3 g (74.1%) of 2b, m.p. 82-84℃ (Lit.[13] m.p. 84℃). IR(KBr): 3455(OH), 1698(CO) cm^{-1}. ^{1}H NMR(δ, ppm): 1.27[m, 26H, $(CH_2)_{13}$], 2.30(t, 2H, CH_2COO), 3.60(t, 2H, CH_2O), 5.34(s, 1H, O*H*, D_2O exchangeable), 11.6(s, 1H, COO*H*, D_2O exchangeable).

15-Acetoxypentadecanoic acid 3b:

According to Lit.[10], 25.8 g(100 mmol) of 2b was converted into 22g (73.5%) of 3b. IR(KBr): 1739, 1712(CO), 1235, 1047 (CH_3COO) cm^{-1}. ^{1}H NMR(δ, ppm): 0.95[m, 26H, $(CH_2)_{13}$], 2.04(s, 3H, $COCH_3$), 2.34(t, 2H, CH_2COO), 4.03(t, 2H, OCH_2), 11.7(s, 1H, COO*H*, D_2O exchangeable).

11-Dodecen-1-ol acetate 4a[14]:

13-Acetoxytridecanoic acid 3a (5.4 g, 20 mmol) and lead tetraacetate(17.7 g, 40 mmol) was added to the mixed solvents of anhydrous benzene (50 mL) and dry pyridine (2 mL) in a 3-necked round-bottom flask with a magnetic stirrer during 15min under stirring, then heated to reflux for 4 h, cooled, diluted with ether (50 mL), filtered through celite and the filterate was subquently washed with 2 M hydrochloric acid (2 × 50 mL), saturated brine and water, dried over anhydrous magnesium sulfate. Solvent removal and distillation gave 4a (1.74 g, 38.5%), b.p. 215-217 ℃/ 15 mmHg. IR(film): 3015(=CH), 1745 (CO), 1240, 1040(CH_3COO), 988, 918($CH{=}CH_2$)cm^{-1}. ^{1}H NMR(δ, ppm): 1.26[br, 16H, $(CH_2)_8$], 1.58-1.80(m, 2H, $CH_2C{=}C$), 2.04 (s, 3H, CH_3CO), 4.04(t, 2H, OCH_2), 4.84(dd, J= 5.4 Hz, J = 13 Hz, 2H, $=CH_2$), 6.0(m, 1H, $=CH$). MS(70 ev, m/z): 226(<1%)(M^+), 166(10) ($M^+ - CH_3COOH$).

13-tetradecen-1-ol acetate 4b:

Analogously, 6.0 g(20 mmol) of 3b was converted into 2.1 g (41.0%) of 4b, b.p. 218-220 ℃/ 15 mmHg. IR(film): 3010(=CH), 1751(CO), 1245, 1045 (CH_3COO), 990, 920($CH{=}CH_2$)cm^{-1}. ^{1}H NMR (δ ,ppm): 1.24[br, 20H, $(CH_2)_{10}$], 1.55-1.80(m, 2H, CH_2C=C), 2.10(s, 3H, CH_3CO), 4.15(t,2H,OCH_2),4.82(dd,J = 7 Hz, J = 15 Hz, 2H, =CH_2), 5.90(m, 1H, =CH).MS(70 ev,m/z): 254(<1%)(M^+), 194(8)(M^+ - CH_3COOH).

10-Dodecen-1-ol acetate 5a:

A solution of anhydrous cobalt dichloride (1.3 g, 10 mmol) and triphenylphosphine (7.9 g,30 mmol)in anhydrous THF(80 mL) was cooled to -10℃. Sodium borohydride (0.4 g,10.5 mmol) was added to the solution during 15 min with vigorous stirring under nitrogen, then a solution of anhydrous THF(20 mL) of 4a (4.5 g, 20 mmol) was added, stirred about 4 h. Ether (50 mL) was added and followed by 2 M hydrochloric acid (50 mL), the aqueous phase was then extracted with ether(2 × 30 mL), the combined ethereal layers were washed with saturated brine and water, dried over anhydrous magnesium sulfate, and evaporated to dryness to give a crude oil, n-hexane (2×30 mL) was added to the oil to precipitate the Ph_3PBH_3 complex and most of the Ph_3P.The solvent was evaporated from the filtrate and the residue purification by column chromatograph [silica gel, petroleum ether / EtOAc (10:1)] yielded 5a(3.6 g, 80%). IR(film): 3015(=CH), 1745(CO), 1240, 1040(CH_3COO), 975, 724(C=C)cm^{-1}. 1H NMR(δ , ppm): 1.29[br, 14H,$(CH_2)_7$],1.60(d,3H, CH_3C=),1.90 (m,2H,CH_2C=), 2.03(s, 3H, CH_3CO),4.04(t,2H,OCH_2),5.40(m,2H, CH=CH).MS (70 ev, m/z): 226(<1%)(M^+),166((12) (M^+-CH_3COOH). GC: purity, 90.2%, Z : E = 93.5 : 6.5.

12-tetradecen-1-ol acetate 5b:

Analogously, 5.1 g 20 mmol of 4b was converted into 4.0 g (78.5%) of 5b. IR(film): 3050(=CH),1750(CO),1245,1045(CH_3COO), 970, 720(C=C)cm^{-1}. ^1H NMR(δ , ppm): 1.25[br, 18H,$(CH_2)_9$], 1.63 (d, 3H, CH_3C=),1.95(m, 2H, CH_2C=), 2.04(s, 3H, CH_3CO), 4.05 (t, 2H, OCH_2),5.40(m, 2H, CH=CH). MS(70 ev, m/z): 254(<1%) (M^+),194(10)(M^+-CH_3COOH).GC: purity, 92.5%,Almost (Z)-isomer.

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