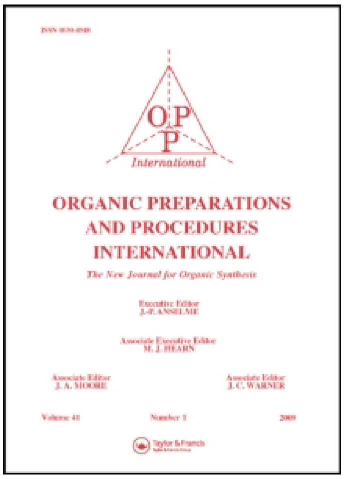

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FACILE SYNTHESIS OF PHEROMONE OF *Dichocrocis Punctiferalis*, A SERIOUS PEST OF SPICES

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The importance of synthetic pheromones in an integrated pest management (IPM) program is well documented.[1] *Dichocrocis punctiferalis* is a serious pest of ginger, cardamom and turmeric. *Konno et al.*[2] have identified its pheromone as a mixture of E- and Z-10-hexadecenal (**6**). In view of the importance of this pheromone in the control of *D. punctiferarlis,* we now report its facile synthesis.

$$\underset{\mathbf{1}}{CH{=}CH(CH_2)_8CO_2H} \xrightarrow{i,\ ii} \underset{\substack{\mathbf{2}\\ a)\ R\,=\,H\quad b)\ R\,=\,CH_3}}{HOCH_2CHOH(CH_2)_8CO_2R} \xrightarrow{iii} \underset{\mathbf{3}}{OHC(CH_2)_8CO_2Me} \xrightarrow{iv}$$

$$\underset{\mathbf{4}}{CH_3(CH_2)_4CH{=}CH(CH_2)_8CO_2Me} \xrightarrow{iv} \underset{\mathbf{5}}{CH_3(CH_2)_4CH{=}CH(CH_2)_8CH_2OH} \xrightarrow{v} \underset{\mathbf{6}}{CH_3(CH_2)_4CH{=}CH(CH_2)_8CHO}$$

i) H_2O_2-HCO_2H, NaOH, H_3O^+ *ii)* MeOH, H^+ *iii)* $NaIO_4$ *iv)* *n*-BuLi, *n*-$C_6H_{13}PPh_3Br$, ether
v) LAH, ether *vi)* PCC, CH_2Cl_2

Peracid hydroxlation[3] of undecenoic acid (**1**, an easily accessible starting material from cracking of castor oil,[4] followed by methylation and oxidative cleavage of the α-glycol function of **2b** yielded aldehyde ester (**3**). Since the pheromone **6** is a mixture of E- and Z-aldehyde, we used the Wittig reaction.[5] Thus, reaction of **3** with the phosphorane of hexyltriphenylphosphonium bromide yielded a ~1:1 E/Z mixture of **4** in 60% yield. Subsequent reduction to the corresponding alcohol **5** followed by PCC oxidation[6] furnished the desired mixture of olefinic aldehydes **6**. The physical and spectroscopic properties of **6**, are consistent with the assigned structure and comparable with the reported[7,8] for similar compounds.

EXPERIMENTAL SECTION

The bps and mps are uncorrected. The IR spectra were recorded on Perkin Elmer Spectrophotometer model 783 as thin film and only pertinent bands are reported (cm^{-1}). The PMR spectra were obtained on a Varian EM 360 instrument (60 MHz) in $CDCl_3$. The GLC analyses were carried out on a 3% OV-17 column under isothermal conditions (temperature 240°) and flow rate 50 mL/ min. All solvents were dried and distilled prior to use unless otherwise noted. Organic extracts were dried over anhydrous Na_2SO_4.

Methyl 10,11-dihydroxyundecanoate (2b).- To a stirred mixture of H_2O_2 (30%, 10 mL) and HCOOH (98%, 20 mL), was added a solution of 10-undecenoic acid (**1**) (9.2 g, 0.05 mol) in formic acid (5 mL). The usual work-up furnished 6.54 g (60%) of the acid as a white solid, mp 87°, lit.[3] mp 84-85°. Its esterification with 5% methanolic hydrochloric acid gave nearly quantitative yield of **2b** as a colorless semi-solid. IR (film): 3450, 2940, 2880, 1750, 1485, 880 and 735 cm^{-1}. PMR ($CDCl_3$): δ 1.33 (m, 14H, 7x -CH_2-), 2.16-2.50 (m, 2H, -CH_2CO_2R), 3.20-3.70 (m, 5H, -CH(OH)-CH_2OH, and two D_2O exchangeable OH), 3.80 (s, 3H,-CO_2CH_3).

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 62.03; H, 10.41. Found: C, 62.12; H, 10.31

Methyl 9-Formylnonanoate (3).- To a stirred suspension of **2b** (2.32 g, 0.01 mol) in 10 mL of CH_3CN and 10 mL of CH_2Cl_2 and 2 mL of H_2O was added sodium periodate (2.2 g, 0.01 mol) in portions and stirring continued for 0.5 hr. The reaction mixture was diluted with diethyl ether, filtered, washed with brine and dried. Removal of solvent under vacuum gave 1.7 g (85%) of the aldehyde ester (**3**) as a colorless oil. bp 119-120°/2 mm, lit.[3] bp 120-121°/3 mm; IR (film): 2950, 2870, 2730, 1750, 1730, 1450, 1210 and 1180 cm^{-1}. PMR ($CDCl_3$): δ 1.1-1.9 (m, 12H, 6 x -CH_2-), 2.0-2.4 (m, 4H, -CH_2CO_2R and -$C\underline{H}_2CHO$), 3.7 (s, 3H, -CO_2CH_3), 9.8 (t, J = 1.5 Hz, 1H, -CHO).

Methyl (E/Z)-10-Hexadecenoate (4).- Wittig salt of *n*-bromohexane (3.74 g, 0.01 mol) was taken in dry ether (50 mL). To the cooled solution (0-5°) under stirring, *n*-butyllithium (6.0 mL, 1.8 M in hexane, 10.0 mmol) was added dropwise under argon atmosphere. After stirring for 1 hr. the orange colored ylide solution was cooled to -40° and the aldehyde (**3**) was added (1.7 g, 8.5 mmol) in ether. Stirring was continued for 1 hr. at -40° and 6 hrs at room temperature. The mixture was acidified with 2N HCl and extracted with diethyl ether. The ethereal layer was washed with water and brine and finally dried. Removal of solvent followed by column chromatography (silica gel, 10% EtOAc in hexane) of the residue afforded 1.36 g (60%) of 4 (as a ~1:1 mixture) as a colorless oil, bp 120°/4 mm; IR (film): 3010, 2930, 2860, 1735, 665, 1465, 1125, 1100, 970 and 720 cm^{-1}. PMR ($CDCl_3$): δ 0.90 (distorted t, 3H, CH_3), 1.39 (s, 18H, 9 x -CH_2-), 2.02-2.50 (m, 6H, 3 x -CH_2-), 3.65 (s, 3H, OCH_3), 5.35 (br. t, 2H, -CH=CH-).

Anal. Calcd. for $C_{17}H_{32}O_2$: C, 76.06. H, 12.01. Found: C, 76.18; H, 12.04

(E/Z)-10-Hexadecen-1-ol (5).- A solution of **4** (1.34 g, 5 mmol) in dry ether was added dropwise to a stirred suspension of LAH (95 mg, 2.5 mm) in ether (100 ml) with stirring at room temperature and the mixture was then refluxed for 1 hr. Excess LAH was decomposed with saturated solution of sodium sulfate, the mixture filtered and the solid washed with diethyl ether. Removal of solvent gave 847 mg (71%) of alcohol **5** as a colorless viscous oil. IR (film): 3310, 3010, 2940, 2860, 1660, 1080, 970 and 740 cm^{-1}. PMR ($CDCl_3$): δ 0.90 (t, 3H, CH_3, J = 6 Hz), 1.30 (br. s, 20 H, 10 x -CH_2-), 1.55 (s, 1H, -OH, D_2O exchangeable), 1.80-2.20 (m, 4H, 2 x -$C\underline{H}_2CH{=}CHC\underline{H}_2$), 3.62 (t, 2H, -$CH_2OH$, J = 6 Hz), 5.39 (br, t, 2H, -CH=CH-).

Anal. Calcd. for $C_{16}H_{32}O$: C, 79.92; H, 13.41. Found: C, 79.78; H, 13.33

(E/Z)-10-Hexadecenals (6).- To alcohol **5** (833 mg, 3.5 mmol) in CH_2Cl_2 (20 mL) was added PCC (900 mg) and the mixture was stirred for 1 hr. After diluting with dry ether (35 mL, the reaction mixture was passed through a small pad of silica gel and concentrated to give 500 mg (61%) of aldehyde **6** as a syrupy liquid, IR (film): 2965, 2740, 1735, 1450, 1360, 1145, 1125, 1080, 1030, 979, 910, 870 and 815 cm^{-1}. PMR ($CDCl_3$): δ 0.90 (distorted t, 3H, CH_3CH_2-), 1.35-1.80 (m, 18H, 9 x -CH_2-), 1.90-2.50 (m, 6H, OHC-$C\underline{H}_2$, -$CH_2CH=CH-C\underline{H}_2$-), 5.37 (m, 2H, -CH=CH-) and 9.84 (t, J = 1.5 Hz, 1H, -CHO); GLC: 3% OV-17 column, 240° flow rate of 50 mL N_2/min., R_t = 10.67 min. (96.3%); TLC (ethyl acetate: pet. ether (20:80), silica gel, DNPH spray): R_f 0.5.

Anal. calcd. for $C_{16}H_{30}O$: C, 80.67; H, 12.60. Found: C, 80.57; H, 12.50

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USEFUL SYNTHESES OF PYRANO- AND PYRIDOINDOLES

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Although isocoumarins (**1**) and isoquinolones (**2**) are well documented in the literature[1,3] their indole analogues of type **3** and **4** have not received much attention. Thus, very few methods have been reported[4,7] for their synthesis. In connection with our work on indole derivatives[8,9] it was decided to synthesize compounds of type **3** and **4**. Reaction of ethyl 1,2-dimethyl-5,6-methylenedioxyindole-3-carboxylate (**6**), obtained in 85% yield by N-methylation of the corresponding indole[8] (**5**), with LDA in THF at -30 to -78° followed by treatment with anisaldehyde (**7a**) gave the hydroxy ester **8a** in 75% yield. The alcohol **8b** was synthesized similarly from **6** in 79% yield using