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# Components of the Sex Pheromone of Chilo Supressalis: Efficient Syntheses of (Z)-11-Hexadecenal and (Z)-13-Octadecenal

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## COMPONENTS OF THE SEX PHEROMONE OF CHILO SUPRESSALIS: EFFICIENT SYNTHESES OF (Z)-11-HEXADECENAL AND (Z)-13-OCTADECENAL

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**ABSTRACT**: (Z)-11-Hexedecenal 1a and (Z)-13-octadecenenal 2a, components of the sex attractant pheromone of *Chilo supressalis*, have been synthesized as their ethylene acetals 1b and 2b from cyclododecanone 3, through intermediacy of the  $C_{12} \omega$  functionalized acetals 8 and 12.

Synthesis of ecologically safe substances for pest control from simple and handy starting materials is one of the prioritary objectives in synthetic chemistry. (Z)-11-Hexedecenal 1a and (Z)-13-octadecenenal 2a are respectively the major and one of the minor components of the sex pheromone of the rice borer (*Chilo Supressalis*)<sup>1</sup>. A number of synthesis of the first aldehyde have been reported <sup>2</sup>,

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but the carbon chain is built up by either alkylation of an alkyne, or copper catalyzed coupling of organomagnesium reagents by either a large number of steps, or from non commercially available



starting compounds. (Z)-13-Octadecenal has been prepared from erucic and tetradecanedioic acids through Wittig reaction as (Z) double bond forming process <sup>3</sup>, and from myristoleic acid through iteration of malonic alkylation <sup>4</sup>. We want to show here that the available in bulk cyclododecanone **3** is a convenient starting material for the synthesis of the above aldehydes.

We considered that adequacy of cyclododecanone as starting material would hinge on its ready conversion to a  $C_{12}$   $\omega$ -functionallized aldehyde. Indeed the acetylenic precursor of acetal 1b could be obtained from the protected  $C_{12}$ acetylenic aldehyde 8, and this would be the result of cleavage of epoxycyclododecanone 5 through pyrolytic fragmentation of the tosylhydrazone of the latter. For the second aldehyde 2a, the acetylenic precursor would derive from the  $C_{12}$   $\omega$ -bromoaldehyde 12, which should be easily obtained from nitrocyclododecanone through retroaldol cleavage.

In our hands conversion of cyclododecanone to cyclododecenone by palladium acetate, according to the method described by Tsuji <sup>5</sup>, led to mixtures of starting and unsaturated ketones. However, we have achieved higher yields than reported by Fujita <sup>6</sup> (55% pure material, instead of 34%) for the same conversion by bromination and dehydrobromination of the ethylene acetal of the starting ketone. Pyrolysis of the tosylhidrazone of the epoxi ketone **6** when performed according to the conditions described by Eschenmoser <sup>7</sup>, or with silica-gel as acid catalyst <sup>8</sup>, led to complex mixtures where only traces of the acetylenic aldehyde



i) Ethylene glycol, benzene, p-TsOH (cat.), reflux 48h; ii) Br<sub>2</sub>, dry ethyl ether, 0°C; iii) t-BuOK, DMSO; iv) acetone, p-TsOH (cat.); v) H<sub>2</sub>O<sub>2</sub>, NaOH 4M, MeOH; vi) 4-phenylsemicarbazide, dry AcOEt; vii) Pb(OAc)<sub>4</sub>, dry CH<sub>2</sub>Cl<sub>2</sub>, 0°C; viii) Ethylene glycol, p-TsOH (cat.), 120°C; ix) 1. BuLi, THF, 2. 1-bromobutane, HMPA; x) H<sub>2</sub> 1 atm, Pd/CaCO<sub>3</sub> Quinoline.

#### Scheme 1

could be observed. However, satisfactory conditions were established for the related thermal fragmentation of the 2-phenylimino- $\Delta^3$ -1,3,4-oxadiazoline derived from the  $\alpha$ , $\beta$ -epoxicarbonylic compound <sup>9</sup>. The phenylsemicarbazone **6** was oxidized with Pb(OAc)<sub>4</sub> in excellent yield to give the 2-phenylimino- $\Delta^3$ -1,3,4-oxadiazoline 7 as a 3:1 diastereomeric mixture, which was used without resolution. Temperature, solvent and catalyst proved critical for this fragmentation. Best results were obtained at 120°C, in ethylene glycol, with a catalytic amount of p-toluenesulfonic acid. No conversion occurred below 120°C, and partial recovery of the unsaturated ketone **4** was found above that temperature. On the other hand, poor yields of mixtures of acetal **8** and unprotected aldehyde resulted when thermolyses were carried out without acid catalyst, or in dry ethylene glycol.

Cyclododecanone is easily converted to the 12-nitrododecanol 10 by reductive retro aldol cleavage of the 2-nitroketone, according to the procedure described by Ballini 10. Nef reaction performed in the presence of ethylene glycol afforded the 2- $\omega$ -hydroxyalkyldioxolane 11, which led to the bromo acetal 12.



i) Isoprenyl acetate, p-TsOH (cat.), reflux 1h; ii) Ac<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> (cat.), AcH/HNO<sub>3</sub>, 0°C;
iii) CH<sub>3</sub>CN / H<sub>2</sub>O, NaBH<sub>4</sub>; iv) 1 MeONa/MeOH; 2 Ethylene glycol, H<sub>2</sub>SO<sub>4</sub>;
v) dry Et<sub>3</sub>N, dry CH<sub>2</sub>Cl<sub>2</sub>, TsCl, 0°C; vi) dry acetone, LiBr, reflux 2h; vii) 1. BuLi, THF, 2. 1-bromobutane, HMPA; x) H<sub>2</sub> 1 atm, Pd/CaCO<sub>3</sub> Quinoline

#### Scheme 2

For both alkylations, that of the acetylene 8 with bromobutane and that of hexyne with the bromo acetal 12 HMPA or dimethylimidazolidindione (DMI) was required as co-solvent. Hydrogenation of the  $C_{16}$  or  $C_{18}$  acetylenic acetals with Lindlar catalyst gave the *cis* ethylenic acetals 1b and 2b.

As a conclusion, we think that the present findings provide valuable methods for preparation of the acetylenic and bromo ethylene acetals 8 and 12 from cyclododecanone 3, and hence of the two components of the sex attractant pheromone of *Chilo supressalis* 1a and 2a. The synthesis of the acetal 2b here described certainly improves former procedures for (Z)-13-octadecenal 2a.

#### **EXPERIMENTAL**

M.p.s were determined with a Reichert apparatus and are uncorrected. IR spectral data were obtained for liquid film or KBr discs, with a Perkin-Elmer 281 spectrophotometer. NMR spectra were recorded for CDCl<sub>3</sub> solutions, with a Varian Unity 300 or Unity 400 spectrometer. Elemental analyses were determined by "Servicio de Semimicroanálisis del Centro de Investigación y Desarrollo (CSIC)

de Barcelona". Silica gel Merck 60 (0.06-0.20 mm) was used for column chromatography, and Silica gel Merck 60 (230-400 mesh) for flash column chromatography, with hexane/ether mixtures as eluent. Ethyl eter and tetrahydrofuran (THF) were distilled from blue sodium diphenylketyl, immediatelly before use.

13-Oxabicyclo[10.1.0]tridecan-2-one 5.- To a stirred mixture of 2-cyclododecenone 4 (1.3 g, 7.2 mmol), methanol (7.2 ml) and 33% hydrogen peroxide (2.1 ml), 4 M aqueous sodium hydroxide (1 ml) was added dropwise, over a period of 10 min under ice-bath cooling. Stirring was continued for another 1 h at room temperature, and the mixture was then poured into water (10 ml), and extracted with ethyl ether (3 x 10 ml). The combined organic layers were washed with water, 5% aqueous iron (II) sulfate, water, and dried. Evaporation of the solvent yielded 13-oxabicyclo[10.1.0]tridecan-2-one as a colorless oil (0.93 g);  $v_{max}$  (NaCl) 2900, 2850, 1700, 1420 and 1270 cm<sup>-1</sup>;  $\delta_{H}$  3.5 (1 H, d, J 2 Hz, 1-H), 2.99 (1 H, ddd, J 2, 2.6 and 9.8 Hz, 12-H), 2.89 (1 H, ddd, J 4, 8 and 14 Hz, 3-H), 2.4-2.3 (1 H, m, 3-H), 2.21 (1 H, m, 11-H) and 1.9-1.1 (12 H, m, -(CH<sub>2</sub>)<sub>6</sub>) ppm;  $\delta_{C}$  207.0 (C<sub>2</sub>), 61.4 (C<sub>1</sub>), 59.1 (C<sub>12</sub>), 41.2 (C<sub>3</sub>), 32.0, 26.7, 26.4, 25.6, 25.4, 24.2, 23.9 and 23.0 ppm. Found: C, 73.20; H, 10.28. C<sub>12</sub>H<sub>20</sub>O<sub>2</sub> requires C, 73.48; H, 10.28 %.

4-Phenylsemicarbazone of 13-Oxabicyclo[10.1.0]tridecan-2-one 6.- A solution of epoxiketone 5 (0.85 g, 4.3 mmol) and 4-phenylsemicarbazide (0.85 g, 4.3 mmol) in ethyl acetate (40 ml) was stirred for 20 h. A white precipitate of 6 (1.1 g) was filtered off, washed with ethyl acetate, and crystallized from chloroform to give white prisms of 4-phenylsemicarbazone of 13-oxabicyclo[10.1.0]tridecan-2-one, m. p. 154-156°C (dec.);  $v_{max}$  (KBr) 3340, 3190, 3080, 2920, 1680, 1590, 1525, 1460, 890, 750 and 690 cm<sup>-1</sup>;  $\delta_{\rm H}$  8.27 (1 H, s, N-H), 8.19 (1 H, s, N-H), 7.6-6.9 (5 H, m, Ph-), 3.26 (1 H, d, J 1.8 Hz, 1-H), 3.1-2.4

(1 H, m, 12-H), 2.5-2.2 (4 H, m, 3-H and 11-H) and 1.8-1 (14 H, m,  $-(CH_2)_{7^-}$ ) ppm;  $\delta_C$  153.1, 148.1, 137.8 (Ph), 128.9 (Ph), 123.4 (Ph), 119.7 (Ph), 61.4 (C<sub>1</sub>), 59.3 (C<sub>12</sub>), 31.8 (C<sub>3</sub>), 26.4, 26.3, 26.1, 24.8, 24.2, 23.3 and 22.7 ppm. Found: C, 69.20; H, 8.17; N, 12.73. C<sub>19</sub>H<sub>27</sub>O<sub>2</sub>N<sub>3</sub> requires C, 69.27; H, 8.26; N, 12.75 %.

2-Phenylimino-∆3-1,3,4-oxadiazoline of 13-Oxabicyclo[10.1.0]tridecan-2-one 7.- A solution of lead tetraacetate (1.4 g, 3.2 mmol) in dry dichloromethane (10 ml) was added dropwise at 0°C to the semicarbazone 6 (0.99 g, 3 mmol) in dry dichloromethane (20 ml). The mixture was stirred at 0°C for 3.5 h, diluted with cold water (6 ml) and stirred for other 1.5 h. The reaction mixture was filtered through Celite, the organic layer separated, and the aqueous layer extracted with dichloromethane. The combined organic layers were washed with water and dried. Evaporation of the solvent give a yellow solid material (0.87 g), which on crystallization from ethyl acetate afforded an about 3:1 stereoisomeric mixture of 2-phenylimino- $\Delta^3$ -1,3,4-oxadiazoline of 13-oxabicyclo[10.1.0]tridecan-2-one as yellow prisms, m.p. 132-134°C; v<sub>max</sub> (KBr) 3060, 2940, 2860, 1690, 1470, 750 and 690 cm<sup>-1</sup>;  $\delta_{\rm H}$  7.5-7.2 (5 H, m, Ph-), 3.48 (1 H, d, J 2.4 Hz, 1-H), 3.4 (1 H, m, 12-H), 3.3 (1 H, d, J 2.1 Hz, 1-H), 2.96 (1 H, m, 12-H) and 2.4-1 (18 H, m, -(CH<sub>2</sub>)<sub>9</sub>-) ppm; δ<sub>C</sub> 159.2, 142.8, 128.92, 128.86, 126.7, 126.6, 124.7, 124.5, 123.7, 122.5, 59.0, 57.2, 57.1, 56.8, 34.2, 31.9, 30.5, 30.4, 26.7, 26.5, 26.2, 25.51, 25.47, 24.0, 23.62, 23.61, 23.1, 21.5 and 21.1 ppm. Found: C, 69.73; H, 7.69; N, 12.85. C<sub>19</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub> requires C, 69.70; H, 7.70; N, 12.83 %.

11-Dodecynal Ethylene Acetal 8.- Oxadiazoline 7 (85 mg, 0.26 mmol), ethylene glycol (16 ml) and p-toluenesulfonic acid monohydrate (5 mg) were heated at 120°C, under argon atmosphere, for 10 min. The reaction mixture was then diluted with water (20 ml), and extracted with petroleum ether (3 x 25ml). The organic layer was whased with aqueous sodium bicarbonate and water, and dried. Evaporation of the solvent yielded 11-dodecynal ethylene acetal (40.2 mg) as a yellow oil (Lit.<sup>11,12</sup>);  $v_{max}$  (NaCl) 3290, 2920, 2850, 1455, 1430, 1130 and 1030 cm<sup>-1</sup>; 4.8 (1 H, t, J 4.8 Hz, 1-H), 4-3.8 (4 H, m, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 2.17 (2 H, dt, J 2.8 and 8.6 Hz, 10-H), 1.93 (1 H, t, J 2.8 Hz, 12-H) and 1.7-1.2 (16 H, m, -(CH<sub>2</sub>)<sub>8</sub>-) ppm;  $\delta_{C}$  104.6 (C<sub>1</sub>), 84.8 (C<sub>11</sub>), 68 (C<sub>12</sub>), 64.8, 33.8 (C<sub>2</sub>), 29.5, 29.4, 29.3, 29.0, 28.7, 28.4, 24.3 (C<sub>10</sub>) and 18.3 (C<sub>3</sub>) ppm.

11-Hexadecynal Ethylene Acetal 9.- To a solution of acetylene 8 (38 mg, 0.17 mmol) in dry THF (0.4 ml), n-butyllithium (0.3 ml, 1.6 M solution in hexane) was added dropwise at room temperature under argon atmosphere. The mixture was stirred for 15 min and then a solution of 1-bromobutane (38 mg, 0.17 mmol) in HMPA (0.25 ml) was added dropwise, and the solution stirred for other 3.5 h. The mixture was diluted with water and extracted with ethyl ether. The organic layer was washed with brine, water, and dried. The solvent was evaporated to give a crude yellow oil. Purification by HPLC gave 11-hexadecynal ethylene acetal (47.6 mg) as a colorless oil;  $v_{max}$  (NaCl) 2920, 2850, 1450, 1400, 1125 and 1030 cm<sup>-1</sup>;  $\delta_{\rm H}$  4.84 (1 H, t, J 5 Hz, 1-H), 4-3.8 (4 H, m, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 2.1 (4 H, m, 10-H and 13-H), 1.8-1.1 (20 H, m, -(CH<sub>2</sub>)<sub>10</sub>-) and 0.89 (3 H, t, J 7 Hz, 16-H) ppm;  $\delta_{\rm C}$  104.6 (C<sub>1</sub>), 80.14 (C<sub>11</sub> or C<sub>12</sub>), 80.11 (C<sub>11</sub> or C<sub>12</sub>), 64.8, 33.8, 31.2, 29.5, 29.3, 29.3, 29.1, 28.8, 24.0, 21.9, 18.7, 18.4 and 13.6 (C<sub>16</sub>) ppm. Found: C, 77.71; H, 11.88. C<sub>20</sub>H<sub>36</sub>O<sub>2</sub> requires C, 77.87; H, 11.76 %.

(Z) 11-Hexadecenal Ethylene Acetal 1b.- A mixture of Lindlar catalyst (1.8 mg), quinoline (0.02 ml) and acetylene 9 (100 mg, 0.36 mmol) in hexane (2 ml) was stirred under hydrogen at 1 atm for 1 h. The mixture was poured into a flash chromatography column and washed with hexane-ethyl ether (24:1). Evaporation of the solvent yielded (Z) 11-hexadecenal ethylene acetal 1b (74 mg) as a yellow oil (Lit.<sup>13</sup>);  $v_{max}$  2920, 1460 and 1030 cm<sup>-1</sup>;  $\delta_{\rm H}$  5.3 (2 H, m, 11-H and

12-H), 4.8 (1 H, t, J Hz, 1-H), 4-3.8 (4 H, m, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 2.0 (4 H, m, 10-H and 13-H), 1.7-1.2 (20 H, m, -(CH<sub>2</sub>)<sub>10</sub>-) and 0.9 (3 H, t, J 3.4 Hz, 16-H) ppm;  $\delta_{\rm C}$  129.87 (C<sub>11</sub> or C<sub>12</sub>), 129.82 (C<sub>11</sub> or C<sub>12</sub>), 104.7 (C<sub>1</sub>), 64.8, 33.9, 31.9, 29.7, 29.54, 29.52, 29.49, 29.3, 27.2, 26.9, 24.1, 22.3 and 13.99 (C<sub>16</sub>) ppm.

12-Hydroxydodecanal Ethylene Acetal 11.- A mixture of H<sub>2</sub>SO<sub>4</sub> (2 ml) and ethylene glycol (15.5 ml) was added dropwise to a stirred solution of 12nitrododecanol 10 (113 mg, 0.49 mmol) in a 5 N solution of MeONa in MeOH (2 ml) at -20°C. Benzene (15 ml) was added and the mixture heated under reflux for 22 h in a Dean-Stark apparatus. The reaction mixture was then extracted with ethyl ether (2 x 25 ml), the organic extract washed with aqueous 1 N NaOH (2 x 25 ml) and dried. Evaporation of solvent yielded 12-hydroxydodecanal ethylene acetal (101 mg) as a white solid, m.p. 36-39°C;  $v_{max}$  3600-3200, 2920, 2850, 1450, 1430, 1130 and 1030 cm<sup>-1</sup>;  $\delta_{\rm H}$  4.81 (1 H, t, J 4.8 Hz, 1-H), 4.00-3.80 (4 H, m, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 3.61 (2 H, t, J 6.5 Hz, 12-H), 1.60 (2 H, q, J 4.8 Hz, 2-H), 1.54 (2 H, q, J 6.5 Hz, 11-H) and 1.40-1.24 (16 H, m, -(CH<sub>2</sub>)<sub>8</sub>-) ppm;  $\delta_{\rm C}$  104.6 (C<sub>1</sub>), 64.8 (-O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 63.0 (C<sub>2</sub>), 33.8 (C<sub>2</sub>), 32.7 (C<sub>11</sub>), 29.51, 29.47, 29.42, 29.35, 25.66 and 24.04 ppm.

12-p-Toluensulfonyloxydodecanal Ethylene Acetal.- Dry triethylamine (0.3 ml, 2.05 mmol) and a solution of p-toluensulfonyl chloride (393 mg, 2.05 mmol) in dry dichloromethane (1 ml) were added, under argon atmosphere, at 0°C, to a solution of hydroxy acetal 11 (336 mg, 1.37 mmol) in dry dichloromethane (4 ml). The mixture was stirred at room temperature for 23 h and then filtered through Celite and washed with dichloromethane (10 ml). The resulting solution was passed through a column of potassium carbonate. Evaporation of solvent gave an orange solid (693 mg) which was purified by flash column chromatography with hexane:diethyl ether (9:1) as eluent, and 12-p-toluensulfonyloxydodecanal ethylene acetal (389 mg) was obtanied as a white solid, m.p. 48-52°C (hexane);  $v_{max}$  2923, 2859, 1603, 1469, 1356, 1176, 952 and 830 cm<sup>-1</sup>;  $\delta_{H}$  7.78 (2 H, d, J 7.8 Hz, Ar), 7.34 (2 H, d, J 8.4 Hz, Ar), 4.84 (1 H, t, J 4.8 Hz, 1-H), 4.01 (2 H, t, J 8.0 Hz, 12-H), 3.96-3.82 (4 H, m, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 2.45 (3 H, s, -CH<sub>3</sub>) and 1.68-1.21 (20 H, m, -(CH<sub>2</sub>)<sub>10</sub>-) ppm;  $\delta_{C}$  129.77, 127.86, 104.67, 70.68, 64.81, 33.88, 29.48, 29.41, 28.89, 25.30, 24.06 and 21.62 ppm. Found: C, 63.46; H, 8.57; S, 7.90.  $C_{21}H_{34}SO_5$  requires C, 63.29; H, 8.60; S, 8.04 %.

**12-Bromododecanal Ethylene Acetal 12.**- A mixture of 12-ptoluensulfonyloxydodecanal ethylene acetal (156 mg, 0.39 mmol), dry lithium bromide (95 mg, 1.09 mmol) and dry acetone (4 ml) was heated under reflux for 75 min. The solvent was evaporated, ethyl ether was added to the residue, and the solution was washed with water (25 ml) brine (2 x 25 ml) and dried. Evaporation of the solvent gave 12-bromododecanal ethylene acetal **12** as a yellow oil (112 mg);  $v_{max}$  2925, 2854, 1463, 1409, 1130 and 1030 cm;  $\delta_{\rm H}$  4.84 (1 H, t, J 4.8 Hz, 1-H), 3.97-3.84 (4 H, m, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 3.40 (2 H, t, J 7.2 Hz, 12-H), 1.85 (2 H, q, J 7.2 Hz, 11-H) and 1.63-1.26 (18 H, m, -(CH<sub>2</sub>)<sub>9</sub>-) ppm;  $\delta_{\rm C}$  104.67 (C<sub>1</sub>), 64.79 (-O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 33.97, 33.89, 32.82, 29.50, 29.48, 29.45, 29.42, 29.37, 28.72, 28.15 and 24.04 ppm. Found: C, 54.32; H, 8.71; Br, 26.32. C<sub>14</sub>H<sub>27</sub>BrO<sub>2</sub> requires C, 54.72; H, 8.86; Br, 26.00 %.

13-Octadecynal Ethylene Acetal 13.- To a solution of 1-hexyne (0.05 ml, 0.44 ml) in dry THF (0.30 ml), n-butyllithium (0.27 ml, 1.6 M solution in hexane) was added dropwise. The mixture was stirred for 10 min and then a solution of 12 (74 mg, 0.24 mmol) in 1,3-dimethyl-2-imidazolidinone (0.5 ml). After 5 h the reaction mixture was poured into ice water (20 ml) and extracted with ethyl ether (4 x 20 ml). The organic layer was washed with brine (2 x 20 ml) and dried. The solvent was evaporated to give a orange oil (95 mg), which was purified by flash

column chromatography with hexane:diethyl ether (9:1) to gave 13-octadecynal ethylene acetal **13** (63 mg) as a yellow oil;  $v_{max}$  2927, 2860, 1458, 1137 and 1040 cm<sup>-1</sup>;  $\delta_{\rm H}$  4.82 (1 H, t, J 4.8 Hz, 1-H), 4.00-3.80 (4 H, m, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 2.11 (4 H, m, 12-H and 15-H), 1.65-1.24 (24 H, m, -(CH<sub>2</sub>)<sub>12</sub>-) and 0.88 (3 H, t, J 7.0 Hz, 18-H) ppm;  $\delta_{\rm C}$  129.89 y 129.82 (C<sub>13</sub> and C<sub>14</sub>), 104.68 (C<sub>1</sub>), 64.80 (-O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 33.91, 31.98, 31.95, 29.76, 29.61, 29.54, 29.32, 29.30, 27.21, 27.18, 26.90, 24.09, 22.33 and 13.99 (C<sub>18</sub>) ppm. Found: C, 77.71; H, 11.88. C<sub>20</sub>H<sub>36</sub>O<sub>2</sub> requires C, 77.87; H, 11.76 %.

(Z) 13-Octadecenal Ethylene Acetal 2b.- A mixture of Lindlar catalyst (0.9 mg), quinoline (0.01 ml) and acetylene 13 (55 mg, 0.18 mmol) in hexane (1 ml) was stirred under hydrogen at 1 atm for 1 h. The mixture was poured into a flash chromatography column and washed with hexane-ethyl ether (24:1). The solvent was evaporated to give a yellow oil (48 mg), which was purified by HPLC chromatography to give (Z)-13-octadecynal ethylene acetal (37 mg) as a colorless oil;  $v_{max}$  2925, 2860, 1457, 1335 and 1040 cm<sup>-1</sup>;  $\delta_{\rm H}$  5.33 (2 H, t, J 4.8Hz, 13-H and 14-H), 4.82 (1 H, t, J 4.8 Hz, 1-H), 4.00-3.80 (4 H, m, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 1.99 (4 H, m, 12-H and 15-H), 1.70-1.20 (24 H, m, -(CH<sub>2</sub>)<sub>12</sub>-) and 0.88 (3 H, t, J 7.0 Hz, 18-H) ppm;  $\delta_{\rm C}$  129.89 and 129.82 (C<sub>13</sub> and C<sub>14</sub>), 104.68 (C<sub>1</sub>), 64.80 (-O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 33.91, 31.98, 31.95, 29.76, 29.61, 29.54, 29.32, 29.30, 27.21, 27.18, 26.90, 24.09, 22.33 and 13.99 (C<sub>18</sub>) ppm. Found: C, 77.20; H, 12.33. C<sub>20</sub>H<sub>38</sub>O<sub>2</sub> requires C, 77.36; H, 12.33 %.

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