



EXO- AND ENDOHORMONES. XXV. <sup>1</sup>  
SYNTHESIS OF AN ISOMERIC MIXTURE  
OF (8E,10Z)-8,10-TETRADECADIEN-1-AL, SEXUAL ATTRACTANT  
FOR HORSE CHESTNUT LEAFMINER *CAMERARIA OHRIDELLA*  
(LEPIDOPTERA, GRACILLARIIDAE)

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A new and practical synthesis of an isomeric mixture of (8E,10Z)-8,10-tetradecadien-1-ol was developed starting from 2-propyn-1-ol. The synthesis was based on a  $C_3+C_3+C_2=C_8$  and  $C_8+C_6=C_{14}$  coupling scheme. The route involves, as the key step, the Grignard-Schlosser cross-coupling reaction. 2,3-dihydro-2H-Pyran was used to protect the -OH function of 2-propyn-1-ol which was added to acrolein and transformed in corresponding acetate. The second coupling reaction of 1-(tetrahydropyranyl)-oxy-4-acetoxy-hex-5-en-2-yne with  $C_2H_5MgBr$  in THF, in the presence of monovalent copper, took place through allylic rearrangement with formation of double bond having Z geometry in ratio of 80%. After hydrogenation with  $LiAlH_4$ , deprotection and acetylation with acetic anhydride of 1-(tetrahydropyranyl)-oxy-oct-4-en-2-yne was obtained (2E,4Z)-2,4-octadien-1-yl acetate. Cross-coupling reaction of (2E,4Z)-2,4-octadien-1-yl acetate with Grignard reagent of 1-(trimethylsilyl)-oxy-6-bromo-hexane in the presence of  $Li_2CuCl_4$  gave (8E,10Z)-8,10-tetradecadien-1-ol, which was oxidated to (8E,10Z)-8,10-tetradecadien-1-al. The mixture of the four geometrical isomers obtained through the synthesis was used in ecological control of the leafminer *Cameraria ohridella*.

## INTRODUCTION

The horse chestnut leafminer *Cameraria ohridella* is the most dangerous pest of horse chestnut *Aesculus hippocastanum* in Southern and Central Europe. The chemical control is difficult because subsequent to eclosion, the larvae penetrate immediately between the folio epidermis in which it starts feeding gnawing a gallery. The pheromonal method is the only efficient one in prognosis, warning and pest control of the *Cameraria ohridella* species and consists in mass trapping by means of traps with sexual synthetic pheromone before copulation. In our country, during the last years it spread with great rapidity creating protection problems of the common ornamental chestnut-tree *Aesculus hippocastanum* L.<sup>2</sup>

(8E,10Z)-8,10-Tetradecadien-1-al was identified by A. Svatos<sup>3</sup> as the female sex pheromone of the horse chestnut leafminer *Cameraria ohridella* (*Lepidoptera, Gracillariidae*).

M. Hoskovec<sup>4</sup> achieved the first synthesis of (8E,10Z)-8,10-tetradecadien-1-al, using Sonogashira<sup>5</sup> cross-coupling reaction, involving the reaction of the terminal alkyne with an organic halide in the presence of a catalytic amount of tetrakis (triphenylphosphine)palladium. The Wittig reaction was used, as the key step, in the synthesis reported by W. Francke<sup>6</sup> ( $C_7+C_3+C_4$ ) and G. Szocs<sup>7</sup> ( $C_8+C_2+C_4$ ). R.M. Figueiredo<sup>8</sup> reported a short synthesis of (8E,10Z)-8,10-tetradecadien-1-al using a combination of two Wittig reaction. J. Grodner<sup>9</sup> reported a stereoselective synthesis of (8E,10Z)-8,10-tetradecadien-1-al which involves the methodology

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based on the Pd(0)-catalyzed cross-coupling of 1-pentynyl magnesium bromide with the corresponding vinyl iodide.

The paper presents a new approach of the (8E,10Z)-8,10-tetradecadien-1-ol synthesis. The route involves, as the key step, the Grignard-Schlosser cross-coupling reaction between an allylic acetate and Grignard reagent of a protected bromo-alcohol.

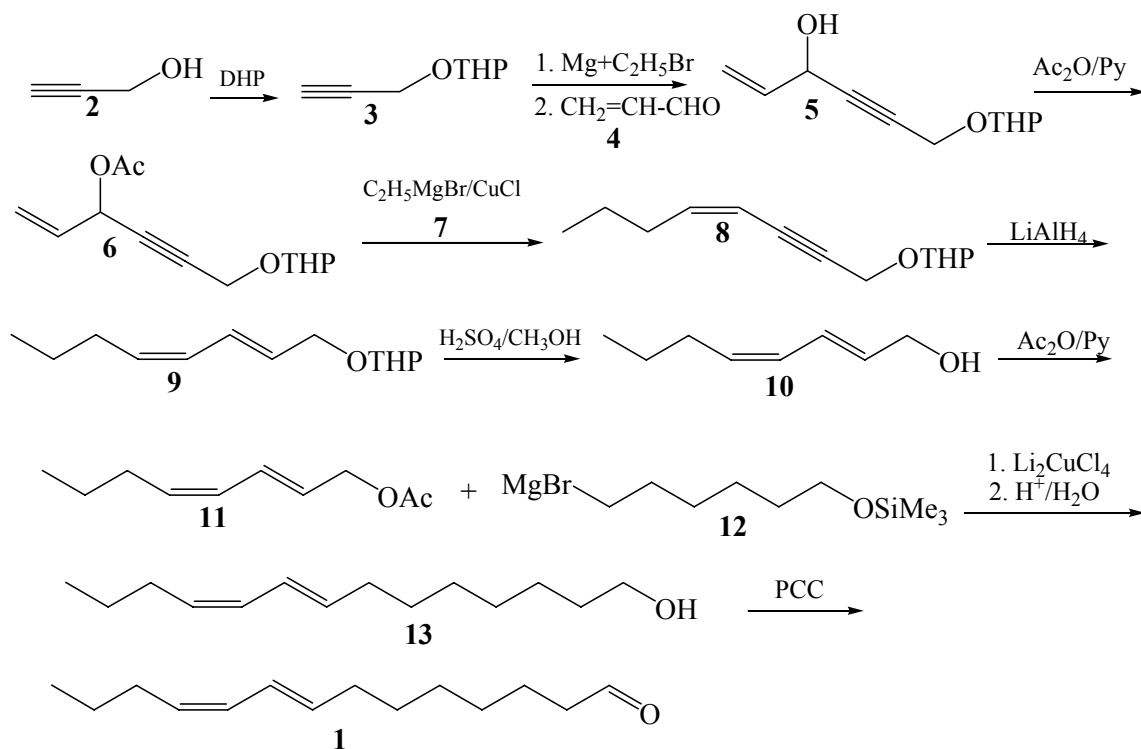
## RESULTS

The synthesis of (8E,10Z)-8,10-tetradecadien-1-ol, the sex pheromone of *Cameraria ohridella* species, was based on a  $C_3+C_3+C_2=C_8$  and  $C_8+C_6=C_{14}$  coupling scheme, starting from 2-propyn-1-ol, using Grignard-Schlosser cross-coupling reaction.<sup>10</sup> 2,3-dihydro-2H-Pyran was used to protect the -OH function of 2-propyn-1-ol (**2**).

1-(tetrahydropyranyl)-oxy-2-Propyne (**3**) through the Grignard reagent was added to acroleine (**4**) forming compound **5** which was transformed in

corresponding acetate **6**. The second coupling reaction of 1-(tetrahydropyranyl)-oxy-4-acetoxyhex-5-en-2-yne (**6**) with  $C_2H_5MgBr$  in THF, in the presence of monovalent copper gave compound **8**. This coupling reaction took place through allylic rearrangement with formation of double bond having Z geometry in ratio of 80%. The other double linkage of the (E,Z) dienic conjugated system was obtained by reduction of the triple bond of compound **8** with  $LiAlH_4$ . 1-(tetrahydropyranyl)-oxy-(2E,4Z)-2,4 Octadiene (**9**) was deprotected and acetylated obtaining (2E,4Z)-2,4-octadien-1-yl acetate (**11**), Scheme 1.

By cross-coupling reaction of (2E,4Z)-2,4-octadien-1-yl acetate (**11**) with Grignard reagent of 1-(trimethylsilyl)-oxy-6-bromo-hexane (**12**) in the presence of  $Li_2CuCl_4$  was obtained (8E,10Z)-8,10-tetradecadien-1-ol (**13**), which was oxidated with PCC to (8E,10Z)-8,10-tetradecadien-1-ol (**1**). The mixture of the four geometrical isomers was obtained through synthesis.



Scheme 1

## DISCUSSION

(2E,4Z)-2,4-Octadien-1-yl acetate (**11**), the key synthon in the synthesis, was checked by means of IR spectrum (film,  $cm^{-1}$ ): 1600 w (C=C), 3000 m

(=C-H), 1000 s (-C-H), 1768 vs (C=O), 1250 s (C-O-C), 1460 m (O-CO-CH<sub>3</sub>) which contains the vibrations characteristic to conjugated diene system and acetoxy group. In the mass spectrum of the (2E,4Z)-2,4-octadien-1-yl acetate (**11**) was

identified the molecular peak to  $m/z=168$ . Other very important fragment appears at  $m/z=43$  ( $\text{CH}_3\text{CO}^+$ ) as base peak, Fig. 1.

(8E,10Z)-8,10-Tetradecadien-1-ol (**13**) results from the reaction between (2E,4Z)-2,4-octadien-1-yl acetate (**11**) and Grignard reagent of 1-(trimethylsilyl)-oxy-6-bromo-hexane (**12**) in the

presence of  $\text{Li}_2\text{CuCl}_4/\text{THF}$  as a catalyst. 1-(trimethylsilyl)-oxy-6-bromo-hexane<sup>11</sup> was obtained from 6-bromo-hexane-1-ol.

The oxidation of (8E,10Z)-8,10-tetradecadien-1-ol (**13**) with PCC gave (8E,10Z)-8,10-tetradecadien-1-al (**1**) with 87% isomeric purity and yield of 70%, Fig. 2.

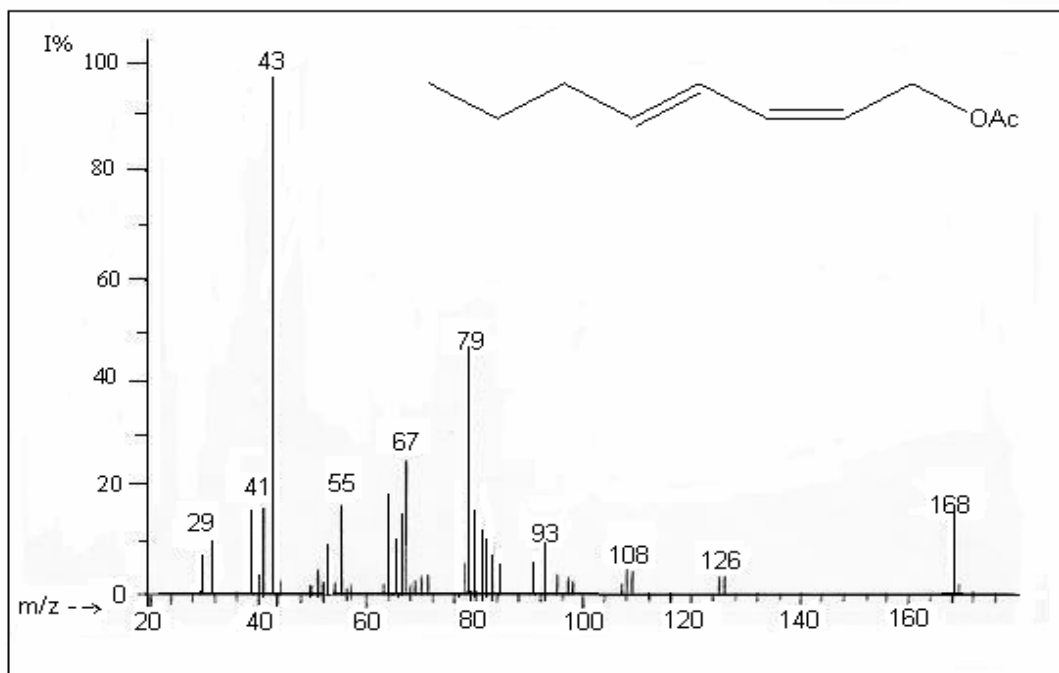


Fig. 1 – Mass spectrum of (2E,4Z)-2,4-octadien-1-yl acetate.

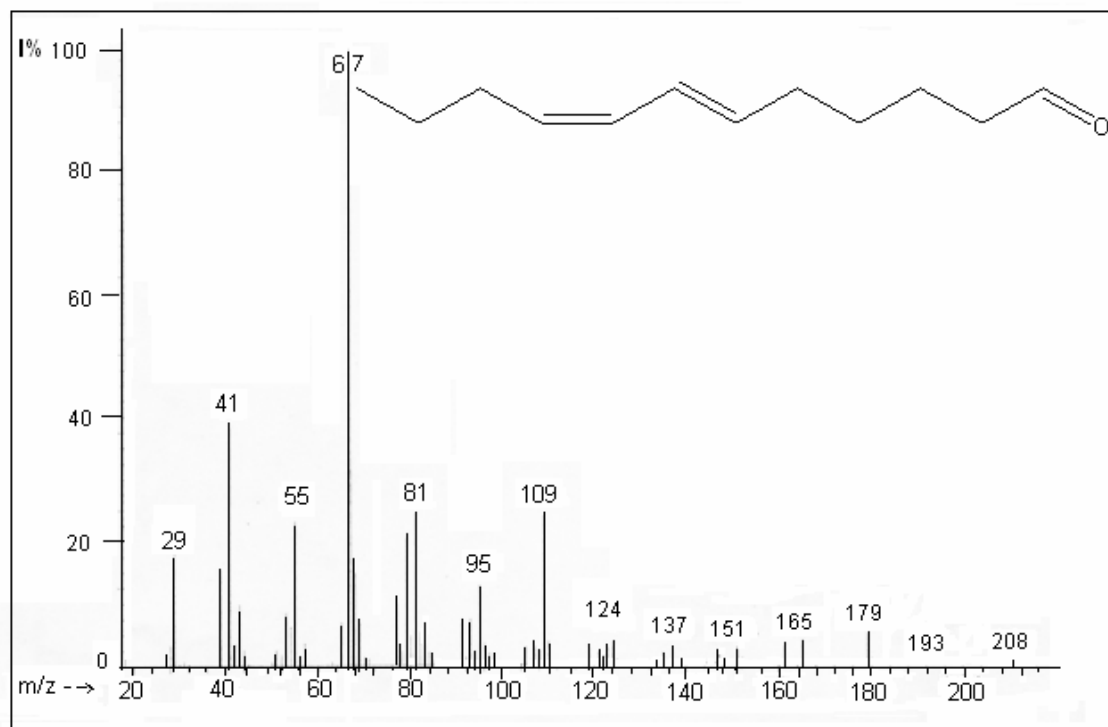


Fig. 2 – Mass spectrum of (8E,10Z)-8,10-tetradecadien-1-al.

The mixture of the four geometrical isomers obtained through the synthesis presents a very good attractivity and selectivity<sup>12</sup> being used in ecological control of the leaves mines *Cameraria ohridella*, the major pest of the ornamental horse chestnut.

## EXPERIMENTAL

GS-MS analysis were performed on a Hewlett Packard GL-MSD 5890-5972 instrument using a HP-5MS 30 m x 0.25 mm capillary column cross linked 5% phenyl methyl silicon 0.25  $\mu\text{m}$ . A Perkin Elmer Spectrometer Model 700 was used for IR spectra. <sup>1</sup>H-NMR (300 MHz) and <sup>13</sup>C-NMR (75 MHz) spectra were recorded at *rt* in CDCl<sub>3</sub> on a Bruker 300 MHz spectrometer, using TMS line as reference.

### 1-(tetrahydropyranyl)-oxy-2-Propyne (3)

To a stirred and cooled at -5<sup>0</sup> C solution of 420 g (5 moles) 2,3-dihydro-2H-pyran and 280 g (0.2 moles) 2-propyn-1-ol in 800 mL chloroform were added 0.6 mL POCl<sub>3</sub> dissolved in 60 mL chloroform. The mixture was stirred 3 hours at room temperature. The reaction mixture was diluted with 800 mL ether and washed with aqueous NaHCO<sub>3</sub> and brine till neutral pH of the washings. After drying over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed and the residue distilled in vacuum. The fraction collected at 67<sup>0</sup>-70<sup>0</sup>/10 mm Hg represented 600 g of 1-(tetrahydropyranyl)-oxy-2-propyne (3). Yield: 85%; GC purity: 99%.

MS (m/z.%): 139(7.76), 101(3.88), 85(100), 82(12.62), 81(10.67), 67(65.04), 57(35.92), 55(52.42), 41(68.93), 39(94.17), 29(52.42).

### 1-(tetrahydropyranyl)-oxy-Hex-5-en-2-yn-4-ol (5)

Under inert atmosphere 140g (1 mole) of 1-(tetrahydropyranyl)-oxy-2-propyne (3) was added at room temperature to a solution of EtMgBr, prepared from 120 g (1.1 moles) of ethyl bromide and 24 g of Mg (1 mole) in 400 mL THF. The reaction mixture was led to completion by stirring 1 hour, cooled at -20<sup>0</sup> and 41.95 g (0.749 moles) of acroleine in 50 mL THF was added dropwise. The reaction mixture was stirred 1 hour and the temperature was raised up to room temperature. After external cooling of reaction mixture with ice a saturated aqueous NH<sub>4</sub>Cl solution was added. The reaction mixture was extracted with diethyl ether. The combined ethereal extracts were successively washed with brine and saturated NaHCO<sub>3</sub> solution and dried over MgSO<sub>4</sub>.

After removal of the solvent were obtained 180g of 1-(tetrahydropyranyl)-oxy-hex-5-en-2-yn-4-ol (5). Yield: 91%; GC purity: 99%.

MS (m/z.%): 195(<1), 112(3.92), 101(24.50), 95(28.43), 85(79.41), 67(100), 57(26.96), 55(71.56), 41(87.5), 39(13.72), 29(45.09).

### 1-(tetrahydropyranyl)-oxy-4-acetoxy-Hex-5-en-2-yne (6)

To a stirred and cooled at -10<sup>0</sup>C solution of 180 g (1 mole) 1-(tetrahydropyranyl)-oxy-hex-5-en-2-yn-4-ol (5) in 260 mL pyridine was added by dropwise 80 mL acetic anhydride. The reaction mixture was kept 24 hours at room temperature and poured into 300 g of crushed ice and extracted with ethylic ether. The combined ethereal extracts were washed with HCl 15%, brine, saturated aqueous NaHCO<sub>3</sub> and brine. After drying over MgSO<sub>4</sub> the extract was concentrated in vacuum obtaining 185 g of 1-(tetrahydropyranyl)-oxy-4-acetoxy-hex-5-en-2-yne (6). Yield: 78%; GC purity: 85%.

MS (m/z.%): 237(<1), 137(10.89), 112(4.95), 101(12.87), 95(93.06), 85(68.31), 78(22.77), 67(34.65), 57(14.85), 43(100), 29(20.79).

### 1-(tetrahydropyranyl)-oxy-Oct-4-en-2-yne (8)

All operation were performed in an inert gas atmosphere. To a stirred and cooled at -20<sup>0</sup>C solution of 175 g (0.784 moles) 1-(tetrahydropyranyl)-oxy-4-acetoxy-hex-5-en-2-yne (6) in 300 mL THF and 3 g CuCl dissolved in 11 mL HMPT was added by dropwise a solution of EtMgBr, prepared from 120 g (1.100 moles) of ethyl bromide and 24 g (1 mole) of Mg in 400 mL THF. The mixture was stirred 2 hours at -20<sup>0</sup>C. At room temperature with external cooling was added by dropwise a saturated aqueous NH<sub>4</sub>Cl solution. The reaction mixture was extracted with diethyl ether and successively washed with brine and saturated NaHCO<sub>3</sub> solution. After drying over MgSO<sub>4</sub> and removal of the solvent were obtained 73 g of 1-(tetrahydropyranyl)-oxy-oct-4-en-2-yne (8). Yield: 58%; GC purity: 64%.

MS (m/z.%): 208(<1), 179(3.94), 165(1.97), 137(2.95), 119(2.46), 107(8.95), 101(26.73), 91(88.66), 85(57.63), 79(100), 65(49.75), 55(31.03), 51(23.64), 43(20.68), 41(55.17), 29(43.34).

### 1-(tetrahydropyranyl)-oxy-(2E,4Z)-2,4-Octadiene (9)

To a stirred solution of 50 g (0.316 moles) of LiAlH<sub>4</sub> in 300 mL THF was added by dropwise at a slow reflux of THF a solution of 60 g (0.288 moles) 1-(tetrahydropyranyl)-oxy-oct-4-en-2-yne (8) in 200 mL THF. The reaction mixture was refluxed 1 hour. After external cooling at -10<sup>0</sup> was added by dropwise 200 mL of ethylic alcohol, 100 mL water and 200 mL H<sub>2</sub>SO<sub>4</sub> 30%. The reaction mixture was extracted with petroleum ether and successively washed with brine and saturated NaHCO<sub>3</sub> solution. After drying over MgSO<sub>4</sub> and removal of the solvent were obtained 38 g of 1-(tetrahydropyranyl)-oxy-(2E,4Z)-2,4-octadiene (9). Yield: 85%; GC purity: 76%.

MS (m/z.%): 210(<1), 109(10.98), 91(4.95), 85(100), 67(55.44), 57(19.8), 41(42.57), 39(18.81), 29(12.87).

### (2E,4Z)-2,4-Octadien-1-ol (10)

A solution of 91 mL CH<sub>3</sub>OH, 13.9 mL water and 2.58 mL H<sub>2</sub>SO<sub>4</sub> was added to 77 g (0.367 moles) of 1-(tetrahydropyranyl)-oxy-(2E,4Z)-2,4-octadiene (9). The reaction mixture was kept 24 hours at room temperature. The reaction development was checked by TLC on silica. The reaction mixture was diluted with brine and was extracted with ethylic ether and successively washed with brine and saturated NaHCO<sub>3</sub> solution. After drying over MgSO<sub>4</sub> the ethereal extract was concentrated in vacuum obtaining 39 g of (2E,4Z)-2,4-octadien-1-ol (10). Yield: 62%; GC purity: 70%.

MS (m/z.%): 126(10.78), 108(5.39), 95(6.86), 93(8.82), 83(63.72), 79(38.23), 70(26.47), 67(67.64), 65(16.66), 55(84.31), 51(16.66), 41(100), 39(60.78), 31(19.60), 29(44.11).

### (2E,4Z)-2,4-Octadien-1-yl acetate (11)

To a stirred and cooled at -10<sup>0</sup>C solution of 33.5 g (0.266 moles) (2E,4Z)-2,4-octadien-1-ol (10) in 67 mL pyridine was added by dropwise 33.5 mL of acetic anhydride. The reaction mixture was kept 24 hours at room temperature. The reaction development was checked by TLC on silica. The reaction mixture was diluted with cool water and extracted with ethylic ether. The ethereal extract was washed with HCl 15%, brine, saturated aqueous NaHCO<sub>3</sub> and brine. After drying over MgSO<sub>4</sub> and the removal of the solvent were obtained 31.3 g of (2E,4Z)-2,4-octadien-1-yl acetate (11). Yield: 70%; GC purity: 65%.

MS (m/z.%): 168(8.91), 125(2.47), 111(2.97), 109(2.47), 93(5.94), 79(34.65), 67(20.79), 66(6.43), 65(5.94), 43(100), 41(16.83), 29(8.91).

(<sup>1</sup>H, RMN, 300Mz, CDCl<sub>3</sub>, δ, ppm): 0.90(H<sub>8</sub>, t, J=7.2 Hz, CH<sub>3</sub>), 1.44(H<sub>7</sub>, m, J=7.2Hz, CH<sub>2</sub>), 2.16(H<sub>6</sub>, q, J=7.2Hz, CH<sub>2</sub>), 5.49(H<sub>5</sub>, dt, J=7.2Hz, CH=CH), 5.96(H<sub>4</sub>, t, J=10.8Hz, CH=CH), 6.23(H<sub>3</sub>, t, J=11Hz, CH=CH), 5.68(H<sub>2</sub>, dt, J=7.8Hz, CH=CH), 4.51(H<sub>1</sub>, d, J=1.38Hz, CH<sub>2</sub>-O), 2.02(H<sub>1</sub>, s, OCOCH<sub>3</sub>)

(<sup>13</sup>C, RMN, 75Mz, CDCl<sub>3</sub>, δ, ppm): 13.85(C<sub>8</sub>, CH<sub>3</sub>), 22.87(C<sub>7</sub>, CH<sub>2</sub>), 28.53(C<sub>6</sub>, CH<sub>2</sub>), 133.82(C<sub>5</sub>, CH=CH) 128.95(C<sub>4</sub>, CH=CH), 131.52(C<sub>3</sub>, CH=CH), 123.71(C<sub>2</sub>, CH=CH), 64.93(C<sub>1</sub>, CH<sub>2</sub>-O), 170.59(C<sub>2</sub>, OCOCH<sub>3</sub>), 20.85(C<sub>1</sub>, OCOCH<sub>3</sub>).

(8E,10Z)-8,10-Tetradecadien-1-ol (**13**)

All operation were performed in an inert gas atmosphere. To a stirred and cooled at -20°C solution of 14.2 g (0.845 moles) (2E,4Z)-2,4-octadien-1-yl acetate and 0.7392 g (3.36 mmoles) Li<sub>2</sub>CuCl<sub>4</sub> in 50 mL of THF was added by dropwise a solution of MgBr(CH<sub>2</sub>)<sub>6</sub>OSi(CH<sub>3</sub>)<sub>3</sub> (**12**), prepared from 3.3 g (0.137 moles) of Mg and 32 g (0.126 moles) of 1-(trimethylsilyl)-oxy-6-bromo-hexane in 150 mL THF:diethyl ether (1:1). The reaction mixture was led to completion by stirring 1 hour at 5°C. A saturated aqueous NH<sub>4</sub>Cl solution and H<sub>2</sub>SO<sub>4</sub> 25% was added by dropwise and the reaction mixture was stirred 1 hour at room temperature. The reaction mixture was extracted with diethyl ether and successively washed with brine and saturated NaHCO<sub>3</sub> solution till neutral pH of the washings. After drying over MgSO<sub>4</sub> and the removal of the solvent were obtained 27 g of compound **13**. The product was purified by column chromatography obtaining 5.7 g of (8E,10Z)-8,10-tetradecadien-1-ol (**13**). Yield: 30%; GC purity: 85%.

MS (m/z.%): 210(10.95), 149(1.42), 135(4.28), 124(7.61), 109(9.52), 95(7.61), 81(46.66), 79(50.47); 77(18.09), 67(100), 55(29.52), 52(46.66), 41(44.76), 39(17.14), 31(31.42).

(8E,10Z)-8,10-Tetradecadien-1-ol (**1**)

In a round bottomed flask fitted with a reflux condenser and mechanical stirrer, 8.8 g (40.74 mmoles) of pyridinium chlorochromate was suspended in 55 mL dichloromethane and 5.7 g (27 mmoles) of (8E,10Z)-8,10-tetradecadien-1-ol (**13**) solved in 15 mL of dichloromethane was added. After 2 hours, 100 mL of dry diethyl ether was added and the supernatant liquid was decanted from a black gum. The insoluble residue was washed with dry diethyl ether. The combined organic solution was washed with brine and dried over MgSO<sub>4</sub>. After removal of the solvent gave 3.8 g of (8E,10Z)-8,10-tetradecadien-1-ol (**1**). Yield: 70%; GC isomeric purity: 87%.

MS (m/z.%): 208(10.37), 137(1.88), 123(2.83), 109(11.32), 107(3.77), 95(19.81), 94(5.66), 93(17.92), 91(15.09), 81(39.62), 79(39.62), 67(100), 55(26.41); 54(15.09); 41(45.28), 39(19.81), 29(27.35).

(<sup>1</sup>H, RMN, 300Mz, CDCl<sub>3</sub>, δ, ppm): 0.92(H<sub>14</sub>, t, J=7.2Hz, -CH<sub>3</sub>), 1.40 (H<sub>13</sub>, m, J=7.5Hz, CH<sub>2</sub>), 2.04(H<sub>12</sub>, H<sub>7</sub>, q, J=7.5Hz, 2X CH<sub>2</sub>), 4.94 (H<sub>11</sub>, t, J=10.5Hz, CH=CH), 5.39 (H<sub>10</sub>, t, J=10.5Hz, CH=CH) 5.67 (H<sub>9</sub>, m, J=7.2 Hz, CH=CH), 5.17 (H<sub>8</sub>, t, J= 8.4 Hz, CH=CH), 1.33 (H<sub>6</sub>, H<sub>5</sub>, H<sub>4</sub>, m, J=6,9, 3xCH<sub>2</sub>), 1.62 (H<sub>3</sub>, s, CH<sub>2</sub>), 2.46 (H<sub>2</sub>, dt, J=7.2Hz, CH<sub>2</sub>-CHO), 9.75 (H<sub>1</sub>, s, CHO).

(<sup>13</sup>C, RMN, 75Mz, CDCl<sub>3</sub>, δ, ppm): 14.11(C<sub>14</sub>,CH<sub>3</sub>), 23.74(C<sub>13</sub>, CH<sub>2</sub>), 28.60(C<sub>12</sub>,CH<sub>2</sub>), 132.12(C<sub>11</sub>, CH=CH), 129.12(C<sub>10</sub>,CH=CH), 128.77(C<sub>9</sub>, CH=CH), 130.7(C<sub>8</sub>, CH=CH), 33.95(C<sub>7</sub>,CH<sub>2</sub>), 31.46(C<sub>6</sub>, CH<sub>2</sub>), 29.57 (C<sub>5</sub>, CH<sub>2</sub>); 29.32(C<sub>4</sub>, CH<sub>2</sub>); 29.12(C<sub>3</sub>, CH<sub>2</sub>), 43.84(C<sub>2</sub>, CH<sub>2</sub>); 203.07(C<sub>1</sub>, CHO).

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