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Synthesis of Insect Juvenile Hormone Analogs, III[1)]

Synthesis of Juvenoids Containing a 2,6-Dienoic Ester Function and a Terminal Pinene Ring System

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The synthesis of 2,6-dienoic ester insect juvenile hormone analogs with a pinene ring in the terminal position is presented.

Synthese von Juvenilhormon-Analogen von Insekten, III[1)]. – Synthese von Juvenoiden mit einer 2,6-Dienestergruppe und einem Pinen-Ring

Es wird die Synthese von 2,6-Dienester-Analogen von Insekten-Juvenilhormonen, die einen Pinen-Ring in der terminalen Stellung enthalten, beschrieben.

Continuing our research on the synthesis of insect juvenile hormone analogs[1)] we synthesized analogs with a pinene ring in the terminal position. Compounds with a pinene ring system and 2,6-dienoic ester functions are widely presented in nature. Therefore we supposed that compounds containing both of the above mentioned moieties would present juvenile activity.

The synthesis was carried out according to a method published by *Mori* and co-workers[2-4)].

Myrtenol (**1**) was the starting material in this synthesis. It was obtained by oxidation of α-pinene with selenium dioxide in anhydrous ethanol to myrtenal[5)] which was subsequently reduced to myrtenol with lithium aluminium hydride. This alcohol was transformed by action of phosphorus tribromide in anhydrous ether into myrtenyl bromide (**2**) in 75% yield. Myrtenyl bromide was subjected then to the condensation reaction with ethyl 3-cyclopropyl-3-oxopropionate (**3**) in the presence of sodium methoxide to produce ethyl 3-oxo-2-(2-pinen-10-yl)-3-cyclopropylpropionate (**4**) in 59% yield. In the NMR spectrum of this compound besides the typical signals of the protons of the pinene function (δ = 0.75 and 1.22 for CH_3-C-CH_3 and δ = 5.16 for C=CH) two signals can be seen at δ = 1.20 (t) and 4.06 (q) which correspond to the protons of the ethyl group in the ester function. A signal at δ = 3.48 (t) in this spectrum is characteristic for 2-H.

The β-keto ester **4** was heated under reflux in water-alcohol solution in the presence of barium hydroxide. As the result of hydrolysis and decarboxylation 1-cyclopropyl-2-(2-pinen-10-yl)ethanone (**5**) was obtained in 85% yield. This ketone was transformed

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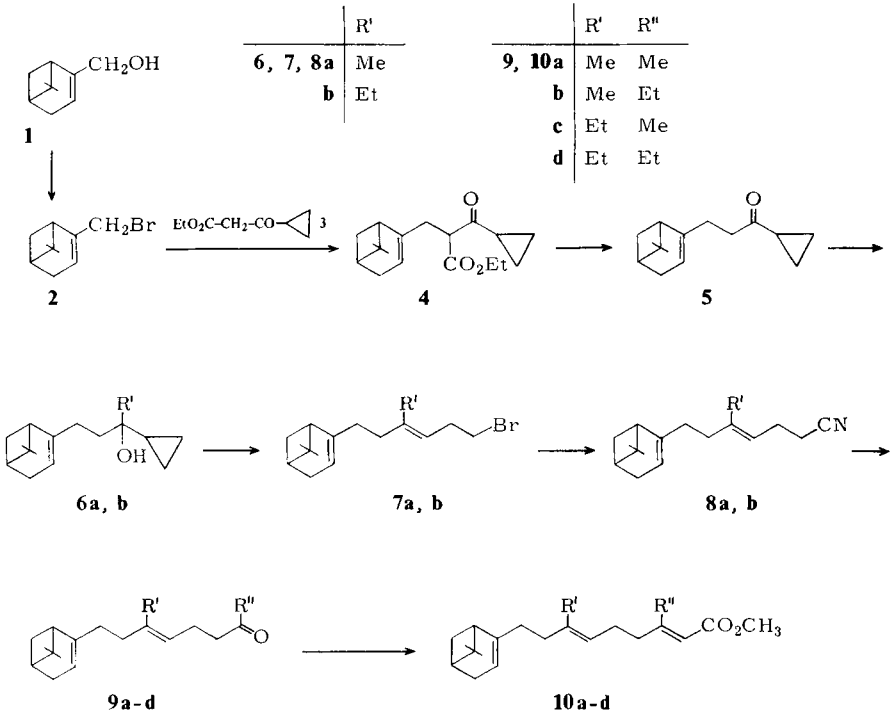

into the hydroxylic derivatives with methyl (**6a**) and ethyl (**6b**) substituents by Grignard reaction with methyl and ethyl magnesium iodides in about 75% yield. In the NMR spectrum of the obtained alcohols appear signals corresponding to the protons of the introduced alkyl groups at $\delta = 1.06$ (s; CH_3) and 1.36 (t; CH_2-CH_3). The obtained alcohols were transformed by the action of 48% hydrogen bromide solution into the unstable bromo derivatives **7a** and **7b**. These compounds without purification were reacted with sodium cyanide in dimethyl sulfoxide solution to produce the nitriles **8a** and **8b** in 73% and 76% yield. In the NMR spectrum of **8a** exists a doublet at $\delta = 1.59$ which is characteristic for the protons of the 4-methyl group. On the other hand a triplet at $\delta = 0.95$ in the NMR spectrum of **8b** indicates the protons of the CH_2-CH_3 group. The ketones **9a** and **9b** were obtained in 60% and 49% yield from **8a** by Grignard reaction with methyl and ethyl magnesium iodide. They present a mixture of stereoisomers in a 3:1 = *E:Z* ratio (GC). Similary, the ketones **9c** and **9d** were prepared from the nitrile **8b** in 47% and 63% yield. In the NMR spectrum of **9a** exists a signal at $\delta = 1.52$ (d) which corresponds to the protons of the 6-methyl group, as well as the characteristic singlet at $\delta = 1.93$ indicating the presence of the CH_3CO group. Similary, for the ketone **9b** a signal at $\delta = 1.51$ for the 7-methyl group protons and a triplet at 0.91 characteristic for the protons of the CH_3-CH_2CO group can be seen. In the spectra of the ketones **9c** and **9d** the signals of the protons of the ethyl group (CH_2-CH_3) exist as triplets at $\delta = 0.88$ (**9c**) and 0.87 (**9d**), respectively. Furthermore, in the case of compound **9c** the signals of the protons of the CH_3CO group are

presented at δ = 1.92 (s). In the spectrum of compound **9d** a triplet at δ = 0.92 corresponds to the protons of the CH_3-CH_2CO group. Each of the ketones **9** was subjected to Wittig-Horner reaction with methyl diethoxyphosphorylacetate in dimethoxyethane solution in the presence of sodium hydride. The obtained four methyl esters **10** (41 – 53% yield) were mixtures of the corresponding stereoisomers with predominant *trans* configuration of the double bond at C-6 in the side chain. In the NMR spectra of the esters **10** the signal at δ = 3.53 (s) is characteristic for the methyl protons of the ester group. A signal at δ = 4.98 (m) corresponds to the olefinic proton at C-6. The olefinic proton at C-2 absorbs at δ = 5.5. The protons of the methyl groups at C-7 (compound **10a** and **10b**) resonate at δ = 1.52 (d) whereas the 3-CH_3 protons of **10a** and **10c** gave signals at δ = 2.07 (d). The protons of the ethyl groups (CH_2-CH_3) localized at C-7 (compound **10c** and **10d**) give signals at δ = 0.89 (t) and the protons connected with C-2 (compound **10b** and **10d**) at δ = 2.48 (t). – The esters **10** are subjected to biological tests.

This work was done within the project MR I-12.1.5.3/2.

Experimental

IR spectra: UR-10 and Specord 71 IR spectrometers. – ^1H NMR spectra: Tesla BS 487C 80 MHz spectrometer, internal standard was hexamethyldisiloxane (HDMSO). – GC: Perkin-Elmer 990 chromatograph; stationary phases: SE 30 (2.5%), PEG 4000 (5%); carrier: Chromosorb G AW DMCS (80 – 100 mesh). – Optical rotations: Polamat A polarimeter.

The following reagents were prepared according to the literature: *Myrtenal*, b.p. 93 – 95 °C/9 Torr, n_D^{20} = 1.5046, $[\alpha]_D^{23}$ = +12.2° (lit.[5] b.p. 68 – 69 °C/4 Torr, n_D^{20} = 1.5040, $[\alpha]_D^{20}$ = +13°). – *Myrtenol* (**1**), b.p. 108 – 110 °C/14 Torr, n_D^{20} = 1.4969, $[\alpha]_D^{24}$ = +36.9° (lit[5] b.p. 77 – 79 °C/3 Torr, n_D^{20} = 1.4968, $[\alpha]_D^{20}$ = +39.6°). – *Myrtenyl bromide* (**2**), b.p. 76 – 78 °C/2 Torr, n_D^{20} = 1.5237, $[\alpha]_D^{27}$ = −29.3° (lit.[6] b.p. 81 °C/1 Torr, n_D^{20} = 1.5234, $[\alpha]_D$ = −29.25°). – *Ethyl 3-cyclopropyl-3-oxopropionate* (**3**), b.p. 80 – 82 °C/6 Torr (lit.[7] b.p. 99 – 101 °C/11 Torr).

Ethyl 3-oxo-2-(2-pinen-10-yl)-3-cyclopropylpropionate (**4**): 42.0 g (0.27 mol) of **3** and then 49.5 g (0.23 mol) of **2** were added dropwise to a cooled solution of sodium ethoxide (prepared from 6.5 g of sodium, 0.28 mol) in 150 ml of dry ethanol and 230 ml of dry benzene. The reaction mixture was refluxed for 2 h. Then the precipitated sodium bromide was dissolved in water and the benzene layer was separated. The aqueous layer was extracted with ether and the combined organic solutions were dried with anhydrous $MgSO_4$. Removal of the solvent under reduced pressure and distillation gave 39.5 g (59%) of **4**, b.p. 169 – 171 °C/2 Torr, n_D^{20} = 1.4938, $[\alpha]_D^{24}$ = +7.2° (*c* = 2.695 in methanol). – IR (film): 1710 (C=O), 1748 cm^{-1} (CO_2). – ^1H NMR (CCl_4): δ = 0.75 (s; 3H, CH_3-C-CH_3), 1.20 (t, *J* = 7 Hz; 3H, CH_3-CH_2), 1.22 (s; 3H, CH_3-C-CH_3), 3.48 (t, *J* = 7 Hz; 1H, $CHCO_2$), 4.06 (q, *J* = 7 Hz; 2H, CH_3-CH_2), 5.16 (m; 1H, C=CH).

$C_{18}H_{26}O_3$ (290.4) Calc. C 74.45 H 9.02 Found C 74.21 H 9.12

1-Cyclopropyl-2-(2-pinen-10-yl)ethanone (**5**): The solutions of 38.5 g (0.13 mol) of **4** in 80 ml of ethanol and 63.0 g (0.2 mol) of $Ba(OH)_2 \cdot 8\,H_2O$ in 250 ml of water were mixed and then refluxed for 18 h under argon. The cooled reaction mixture was poured into water with ice containing hydrochloric acid in order to dissolve the obtained barium carbonate and was then extracted with

ether. The extract was washed with water, $NaHCO_3$ solution, brine, and dried with anhydrous $MgSO_4$. After removing of the solvent, the residue was distilled under reduced pressure to give 25.6 g (86%) of **5**, b.p. 123–125 °C/2 Torr, $n_D^{20} = 1.4979$, $[\alpha]_D^{21} = +30.5°$ ($c = 3.880$ in methanol). – GC: One peak. – IR (film): 1710 cm^{-1} (C=O). – ^1H NMR (CCl_4): $\delta = 0.76$ (s; 3H, CH_3-C-CH_3), 1.22 (s; 3H, CH_3-C-CH_3), 5.10 (m; 1H, C=CH).

$C_{15}H_{22}O$ (218.3) Calc. C 82.52 H 10.16 Found C 82.45 H 10.08

2-Cyclopropyl-1-(2-pinen-10-yl)-2-propanol (**6a**): The solution of 11.3 g (0.052 mol) of **5** in 20 ml of ether was added dropwise at 0 °C to a solution of the Grignard reagent prepared from 3.7 g (0.15 mol) of magnesium and 21.3 g (0.15 mol) of methyl iodide in 100 ml of dry ether. The reaction mixture was stirred for 12 h at room temperature, then poured into saturated NH_4Cl solution with ice, extracted with ether, and dried with anhydrous K_2CO_3. The solvent was removed and the residue was distilled under reduced pressure to give 9.3 g (77%) of **6a**, b.p. 118–122 °C/3 Torr, $n_D^{20} = 1.4992$, $[\alpha]_D^{25} = +30.9°$ ($c = 2.723$ in methanol). – GC: One peak. – IR (film): 3415 cm^{-1} (OH). – ^1H NMR (CCl_4): $\delta = 0.81$ (s; 3H, CH_3-C-CH_3), 1.06 (s; 3H, CH_3), 1.25 (s; 3H, CH_3-C-CH_3), 5.14 (m; 1H, C=CH).

$C_{16}H_{26}O$ (234.4) Calc. C 81.99 H 11.18 Found C 81.66 H 10.80

2-Cyclopropyl-1-(2-pinen-10-yl)-2-butanol (**6b**) was prepared from 12.5 g (0.057 mol) of **5** and 3.7 g (0.15 mol) of magnesium and 23.4 g (0.15 mol) of ethyl iodide as described for the alcohol **6a**. Thus 10.7 g (75%) of **6b** was isolated, b.p. 140–142 °C/2 Torr, $n_D^{20} = 1.4989$, $[\alpha]_D^{25} = +33.1°$ ($c = 2.678$ in methanol). – GC: One peak. – IR (film): 3435 cm^{-1} (OH). – ^1H NMR (CCl_4): $\delta = 0.77$ (s; 3H, CH_3-C-CH_3), 1.22 (s; 3H, CH_3-C-CH_3), 1.36 (t, $J = 7$ Hz; CH_2-CH_3), 5.10 (m; 1H, C=CH).

$C_{17}H_{28}O$ (248.4) Calc. C 82.20 H 11.36 Found C 82.16 H 11.28

5-Bromo-2-methyl-1-(2-pinen-10-yl)-2-pentene (**7a**): 82 ml of a cooled 48% HBr solution was added dropwise at –5 °C to the solution of 16.3 g (0.07 mol) of **6a** in 80 ml of ether. After stirring for 45 min at –5 °C water with ice was added to the reaction mixture and it was extracted with hexane. The extract was washed with $NaHCO_3$ solution, dried with anhydrous $MgSO_4$, and filtered through Al_2O_3. After removing of the solvent the crude bromide was used in the next reaction.

5-Bromo-2-ethyl-1-(2-pinen-10-yl)-2-pentene (**7b**): It was prepared from **6b** as described for the bromide **7a**.

5-Methyl-6-(2-pinen-10-yl)-4-hexenenitrile (**8a**): 20.5 g (0.07 mol) of the crude bromide **7a** was added to the solution of 7.8 g (0.16 mol) of sodium cyanide in 90 ml of dry dimethyl sulfoxide. The mixture was stirred for 1 h at 60 °C and then for 12 h at room temperature. The reaction mixture was poured into water and extracted with hexane. The extract was washed with water, brine, and dried with anhydrous $MgSO_4$. After removing of the solvent the residue was distilled under reduced pressure giving 12.4 g (73%) of **8a**, b.p. 168–172 °C/2 Torr, $n_D^{20} = 1.5012$, $[\alpha]_D^{23} = +15.2°$ ($c = 1.250$ in methanol). – GC: Two peaks (*E* and *Z* isomers, 3:1, respectively). – IR (film): 1642 (C=C), 2245 cm^{-1} (CN). – ^1H NMR (CCl_4): $\delta = 0.78$ (s; 3H, CH_3-C-CH_3), 1.22 (s; 3H, CH_3-C-CH_3), 1.59 (d, $J = 1$ Hz; 3H, CH_3), 5.09 (m; 1H, C=CH).

$C_{17}H_{25}N$ (243.4) Calc. N 5.76 Found N 5.73

5-Ethyl-6-(2-pinen-10-yl)-4-hexenenitrile (**8b**): It was prepared from 21.0 g (0.07 mol) of the crude bromide **7b** as described for the nitrile **8a**. Thus 13.2 g (76%) of **8b** was isolated, b.p. 184–186 °C/2 Torr, $n_D^{20} = 1.5021$, $[\alpha]_D^{15} = +19.6°$ ($c = 1.220$ in methanol). – GC: Two peaks (*E* and *Z* isomers, 3:1, respectively). – IR (film): 1640 (C=C), 2245 cm^{-1} (CN). – ^1H NMR

(CCl_4): δ = 0.78 (s; 3H, CH_3-C-CH_3), 0.95 (t, J = 7 Hz; 3H, CH_2-CH_3), 5.03 (m; 1H, C=CH), 5.11 (m; 1H, C=CH).

$C_{18}H_{27}N$ (257.4) Calc. N 5.44 Found N 5.35

6-Methyl-7-(2-pinen-10-yl)-5-hepten-2-one (**9a**): The solution of 5.7 g (0.023 mol) of **8a** in 20 ml of dry benzene was added dropwise at 0°C to a solution of the Grignard reagent prepared from 2.4 g (0.1 mol) of magnesium and 17.0 g (0.12 mol) of methyl iodide in 60 ml of ether. The mixture was refluxed for 8 h and then stirred for 64 h at room temperature. The reaction mixture was poured into ice with water containing hydrochloric acid and extracted with ether. The extract was washed with $NaHCO_3$ solution and dried with anhydrous $MgSO_4$. After removing of the solvent the residue was distilled under reduced pressure to afford 3.7 g (60%) of **9a**, b.p. 162–164°C/6 Torr, n_D^{20} = 1.4971, $[\alpha]_D^{23}$ = +12.1° (c = 1.124 in methanol). – GC: Two peaks (E and Z isomers, 3:1, respectively). – IR (film): 1720 cm^{-1} (C=O). – ^1H NMR (CCl_4): δ = 0.74 (s; 3H, CH_3-C-CH_3), 1.19 (s; 3H, CH_3-C-CH_3), 1.52 (d, J = 1 Hz; 3H, CH_3), 1.93 (s; 3H, CH_3CO), 4.96 (m; 1H, 5-H), 5.07 (m; 1H, C=CH).

$C_{18}H_{28}O$ (260.4) Calc. C 83.02 H 10.84 Found C 82.93 H 10.72

7-Methyl-8-(2-pinen-10-yl)-6-octen-3-one (**9b**): It was prepared from 5.7 g (0.023 mol) of **8a** as described for **9a**. Thus 3.2 g (49%) of **9b** was isolated, b.p. 188–192°C/7 Torr, n_D^{20} = 1.4952, $[\alpha]_D^{23}$ = +11.8° (c = 1.112 in methanol). – GC: Two peaks (E and Z isomers, 3:1, respectively). – IR (film): 1720 cm^{-1} (C=O). – ^1H NMR (CCl_4): δ = 0.74 (s; 3H, CH_3-C-CH_3), 0.91 (t, J = 7 Hz; 3H, CH_2-CH_3), 1.19 (s; 3H, CH_3-C-CH_3), 1.51 (d, J = 1 Hz; 3H, CH_3), 4.96 (m; 1H, 6-H), 5.06 (m; 1H, C=CH).

$C_{19}H_{30}O$ (274.4) Calc. C 83.15 H 11.02 Found C 83.31 H 11.21

6-Ethyl-7-(2-pinen-10-yl)-5-hepten-2-one (**9c**): It was prepared from 10.0 g (0.039 mol) of **8b** as described for **9a**. Thus 5.1 g (47%) of **9c** was isolated, b.p. 138–142°C/7 Torr, n_D^{20} = 1.4962, $[\alpha]_D^{23}$ = +15.5° (c = 1.021 in methanol). – GC: Two peaks (E and Z isomers, 3:1, respectively). – IR (film): 1720 cm^{-1} (C=O). – ^1H NMR (CCl_4): δ = 0.77 (s; 3H, CH_3-C-CH_3), 0.88 (t, J = 7 Hz; 3H, CH_2-CH_3), 1.21 (s; 3H, CH_3-C-CH_3), 1.92 (s; 3H, CH_3CO), 4.93 (m; 1H, 5-H), 5.07 (m; 1H, C=CH).

$C_{19}H_{30}O$ (274.4) Calc. C 83.15 H 11.02 Found C 82.91 H 11.17

7-Ethyl-8-(2-pinen-10-yl)-6-octen-3-one (**9d**): It was prepared from 8.9 g (0.035 mol) of **8b** as described for **9a**. Thus 6.3 g (63%) of **9d** was isolated, b.p. 162–165°C/7 Torr, n_D^{20} = 1.4969, $[\alpha]_D^{24}$ = +14.1° (c = 0.987 in methanol). – GC: Two peaks (E and Z isomers, 3:1, respectively). – IR (film): 1720 cm^{-1} (C=O). – ^1H NMR (CCl_4): δ = 0.74 (s; 3H, CH_3-C-CH_3), 0.87 (t, J = 7 Hz; 3H, CH_2-CH_3), 0.92 (t, J = 7 Hz; 3H, CH_3-CH_2-CO), 1.20 (s; 3H, CH_3-C-CH_3), 4.92 (m; 1H, 6-H), 5.07 (m; 1H, C=CH).

$C_{20}H_{32}O$ (288.5) Calc. C 83.27 H 11.18 Found C 83.12 H 11.09

Methyl 3,7-dimethyl-8-(2-pinen-10-yl)-2,6-octadienoate (**10a**): To a suspension of 0.78 g (0.016 mol) of 50% sodium hydride in 25 ml of dry dimethoxyethane, 3.4 g (0.016 mol) of methyl diethoxyphosphorylacetate was added (under argon), and the mixture was stirred for 1 h at room temperature. Then a solution of 3.5 g (0.013 mol) of **9a** in 10 ml of dimethoxyethane was added dropwise, and the reaction mixture was kept at 55–60°C for 12 h. Subsequently it was poured into water, extracted with ether, and dried with anhydrous $MgSO_4$. After removing of the solvent the residue was distilled under reduced pressure to give 1.75 g (41%) of **10a**, n_D^{20} = 1.5020, $[\alpha]_D^{26}$ = +5.5° (c = 0.548 in methanol). – GC: Four peaks (11.6, 31.8, 44.1, and 12.5%). – IR (film): 1650 (C=C), 1730 cm^{-1} (C=O). – ^1H NMR (CCl_4): δ = 0.75 (s; 3H, CH_3-C-CH_3),

1.20 (s; 3H, CH_3-C-CH_3), 1.52 (d, J = 1 Hz; 3H, 7-CH_3), 2.07 (d, J = 1 Hz; 3H, 3-CH_3), 3.53 (s; 3H, CH_3O), 4.98 (m; 1H, 6-H), 5.07 (m; 1H, C=CH), 5.52 (m; 1H, 2-H).

$C_{21}H_{32}O_2$ (316.5) Calc. C 79.70 H 10.19 Found C 79.51 H 10.01

Methyl 3-ethyl-7-methyl-8-(2-pinen-10-yl)-2,6-octadienoate (**10b**): It was prepared from 2.8 g (0.01 mol) of **9b** as described for **10a**. Thus 1.7 g (50%) of **10b** was isolated n_D^{20} = 1.4997, $[\alpha]_D^{26}$ = +6.3° (c = 0.794 in methanol). – GC: Four peaks (9.9, 42.2, 28.3, and 19.6%). – IR (film): 1650 (C=C), 1730 cm^{-1} (C=O). – ^1H NMR (CCl_4): δ = 0.75 (s; 3H, CH_3-C-CH_3), 1.20 (s; 3H, CH_3-C-CH_3), 1.52 (d, J = 1 Hz; 3H, CH_3), 2.47 (t, J = 7 Hz; 3H, CH_2-CH_3), 3.53 (s; 3H, CH_3O), 4.98 (m; 1H, 6-H), 5.08 (m; 1H, C=CH), 5.53 (m; 1H, 2-H).

$C_{22}H_{34}O_2$ (330.5) Calc. C 79.95 H 10.37 Found C 80.11 H 10.52

Methyl 7-ethyl-3-methyl-8-(2-pinen-10-yl)-2,6-octadienoate (**10c**): It was prepared from 3.3 g (0.012 mol) of **9c** as described for **10a**. Thus 1.8 g (45%) of **10c** was isolated, n_D^{20} = 1.5095, $[\alpha]_D^{26}$ = +7.1° (c = 0.846 in methanol). – GC: Four peaks (11.3, 32.8, 48.2, and 7.7%). – IR (film): 1650 (C=C), 1730 cm^{-1} (C=O). – ^1H NMR (CCl_4): δ = 0.77 (s; 3H, CH_3-C-CH_3), 0.89 (t, J = 7 Hz; 3H, CH_2-CH_3), 1.20 (s; 3H, CH_3-C-CH_3), 2.07 (d, J = 1 Hz; 3H, CH_3), 3.53 (s; 3H, CH_3O), 4.98 (m; 1H, 6-H), 5.08 (m; 1H, C=CH), 5.53 (m; 1H, 2-H).

$C_{22}H_{34}O_2$ (330.5) Calc. C 79.95 H 10.37 Found C 79.69 H 10.32

Methyl 3,7-diethyl-8-(2-pinen-10-yl)-2,6-octadienoate (**10d**): It was prepared from 1.9 g (0.007 mol) of **9d** as described for **10a**. Thus 1.2 g (53%) of **10d** was isolated, n_D^{20} = 1.4959, $[\alpha]_D^{26}$ = +5.9° (c = 0.782 in methanol). – GC: Four peaks (14.8, 38,5, 33.7, and 13.0%). – IR (film): 1650 (C=C), 1730 cm^{-1} (C=O). – ^1H NMR (CCl_4): δ = 0.77 (s; 3H, CH_3-C-CH_3), 0.89 (t, J = 7 Hz; 3H, C-7 CH_2-CH_3), 1.20 (s; 3H, CH_3-C-CH_3), 2.48 (t, J = 7 Hz; 3H, C-3 CH_2-CH_3), 3.53 (s; 3H, CH_3O), 4.98 (m; 1H, 6-H), 5.10 (m; 1H, C=CH), 5.48 (m; 1H, 2-H).

$C_{23}H_{36}O_2$ (344.5) Calc. C 80.18 H 10.53 Found C 80.01 H 10.31

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