Highly stereoselective synthesis of a sex pheromone of the dry bean beetle *Callosobruchus analis*

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Total synthesis of 3-methylhept-2(*Z*)-enoic acid, a sex pheromone of the dry bean beetle *Callosobruchus analis*, has been performed using a previously developed highly stereoselective method of the construction of disubstituted (*Z*)-methylolefins based on the higher thermodynamic stability of (*E*)-isomers of α,β-disubstituted acroleins.

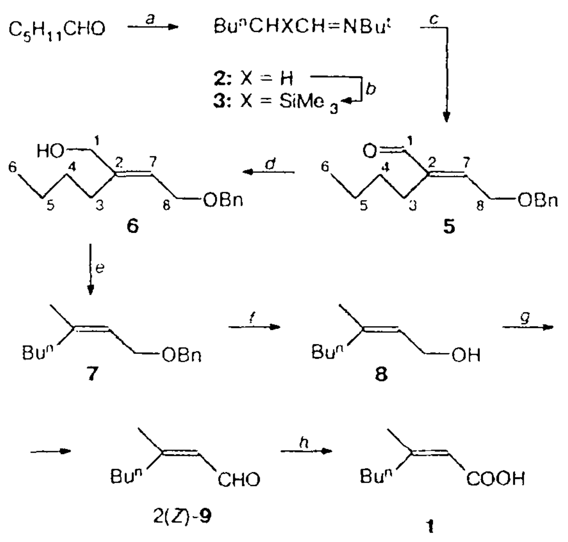
Key words: insect pheromones, stereoselective synthesis, higher thermodynamic stability of (*E*)-isomers of α,β-disubstituted acroleins, 3-methylhept-2(*Z*)-enoic acid, 3-methylhept-2(*Z*)-enol.

Beetles of the *Callosobruchus* genus are the main pests of legumes in tropical and subtropical regions.[1] The first representative of sex pheromones of this beetles, which proved to be 3-methylhept-2(*Z*)-enoic acid (**1**),[2] was isolated in 1991 from glands of *C. analis* females. Although the structure of this compound appears simple, acid **1** has been prepared only as a minor product mixed with its 2(*E*)-isomer;[2,3] and to the best of our knowledge its stereoselective synthesis has not yet been reported.

The present communication fills this gap. To construct **1**, we used the method of highly stereoselective synthesis of disubstituted (*Z*)-methylolefins developed in our previous study,[4] which is based on the fact that the (*E*)-isomers of α,β-disubstituted acroleins are thermodynamically more favorable, and on the possibility of stereospecific transformation of the latter into the corresponding (*Z*)-methylolefins. In conformity with the chosen methodology, as the starting compounds for the synthesis of **1**, we used trimethylsilylimine **3**, which is smoothly formed from hexanal *via* *tert*-butylimine **2**, and benzyl ether of glycolaldehyde (**4**).

The condensation of **4** with the anion of imine **3** (generated from **3** on treatment with LDA) under previously developed conditions[5] gave (*E*)-acrolein (**5**) containing ~5% 2(*Z*)-isomer in a yield of 55% (Scheme 1). This conclusion follows from comparison of the integral intensities of the signals of the CHO-group protons for (*E*)- and (*Z*)-isomers (δ 9.35 and 10.0, respectively) in the ^{1}H NMR spectrum of the sample obtained.[6] The reduction of aldehyde **5** with NaBH$_4$ gave quantitatively allylic alcohol **6**, whose *E*-configuration was confirmed by the data of ^{13}C and ^{1}H NMR spectroscopy, which are in good agreement with the results obtained previously[7] for related systems. Stereospecific reduction of the hydroxymethyl group in **6** to a methyl group was carried out by a known procedure[8] *via* the corresponding sulfate. Debenzylation of the benzyl ether **7** thus obtained on treatment with Li in liquid NH$_3$ gave the corresponding alcohol **8**. The oxidation of this product by MnO$_2$ yielded aldehyde 2(*Z*)-**9**, containing ~10% 2(*E*)-isomer, as follows from comparison of the integral intensities of the signals of the C(3)Me (δ 1.95 and 2.17) and CHO (δ 9.95 and 10.0) groups for (*Z*)- and

Scheme 1*



Reagents: *a*, Bu^{t}NH$_2$; *b*, LDA, Me$_3$SiCl; *c*, LDA, BnOCH$_2$CHO (**4**), H$_3$O$^+$; *d*, NaBH$_4$; *e*, Py · SO$_3$, LiAlH$_4$; *f*, Li/NH$_3$; *g*, MnO$_2$; *h*, Ag$_2$O.

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* The numbering of C atoms given in the Scheme was chosen for convenience in presenting the NMR spectra.

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(*E*)-isomers, respectively, in the ^{1}H NMR spectrum of the resulting sample. Oxidation of the aldehyde mixture obtained by moist silver oxide under standard conditions gives a mixture of target acid **1** with its 2(*E*)-isomer in ~(9 : 1) ratio and in 85% yield; this ratio exactly corresponds to the isomeric composition of the initial aldehyde mixture. Isomerically pure acid **1** was isolated by flash chromatography on SiO_2. Its overall yield amounted to ~10% with respect to aldehyde **4**.

The structures of compounds synthesized for the first time were confirmed by elemental analysis and a set of spectral data (^{1}H and ^{13}C NMR, IR, and mass spectra). In particular, the ^{13}C NMR spectra of compounds **1** and **7—9** exhibit signals at 23—25 and 30—32 ppm (the C(3)$\underline{\mathrm{Me}}$ group and C(4) in the (*Z*)-isomers). In combination with the absence of signals at 15—19 and 40—42 ppm (the C(3)$\underline{\mathrm{Me}}$ group and C(4) in the (*E*)-isomer),[7] this unambiguously confirms that the configurations of these compounds correspond to those presented in the Scheme.

Experimental

The IR spectra were recorded for solutions in CCl_4 or $CHCl_3$ on a Perkin—Elmer 577 instrument. ^{1}H and ^{13}C NMR spectra were measured for $CDCl_3$ solutions on Bruker AC-200 and Bruker WM-250 spectrometers. Mass spectra (EI, 70 eV) were run on a Varian MAT CH-6 instrument. Preparative flash chromatography was carried out on silica gel L [40—100 μm, Chemapol (Czechoslovakia)]; TLC was performed on Silufol plates (Kavalier, Czechoslovakia) in the following solvent systems: hexane—AcOEt (85 : 15 v/v) (A) and hexane—ether (1 : 1 v/v) (B).

The main solvents were purified as follows: THF and ether were kept over KOH, distilled successively from Na and $LiAlH_4$, refluxed under Ar with benzophenone Na ketyl until a persistent blue color appeared, and distilled directly into the reaction vessel. Hexane and benzene were distilled from Na.

The solution of LDA was prepared directly in the reactor from equivalent amounts of Pr^i_2NH and a 1.3—1.5 *M* hexane solution of Bu^nLi, prepared by a standard procedure. The organic extracts were washed by a saturated solution of $MgSO_4$, dried with anhydrous $MgSO_4$, and concentrated *in vacuo* ("The usual workup").

***N*-*tert*-Bultylhexan-1-imine (2) and *N*-*tert*-butyl-2-trimethylsilylhexan-1-imine (3).** A solution of hexanal (Fluka) (9.81 g, 97.7 mmol) in 25 mL of ether was added dropwise to a solution of Bu^tNH_2 (8.6 g, 117.5 mmol) in 50 mL of ether stirred at −10 °C. The mixture was stirred for 2 h at 0 °C, then 2 g of KOH was added, and the mixture was stirred for an additional 0.5 h. The organic layer was separated and dried with K_2CO_3. Evaporation of the solvent and vacuum distillation of the product gave 11.7 g (77.6%) of imine **2**, b.p. 58 °C (8 Torr); n_D^{20} 1.4285. Found (%): C, 76.99; H, 13.49; N, 9.10. $C_{10}H_{21}N$. Calculated (%): C, 77.34; H, 13.54; N, 9.04. ^{1}H NMR, δ: 0.89 (t, 3 H, Me, *J* = 6.7 Hz); 1.17 (s, 9 H, Me_3C); 1.30 (m, 4 H, $H_2C(4)$, $H_2C(5)$); 1.60 (m, 2 H, $H_2C(3)$); 2.20 (dt, 2 H, $H_2C(2)$, J_1 = 5.2 Hz, J_2 = 7.5 Hz); 7.57 (t, 1 H, HC(1), *J* = 5.2 Hz).

A solution of **2** (11.7 g, 75.7 mmol) in 5 mL of THF was added over a period of 30 min to a freshly prepared solution of LDA (79.5 mmol) in 160 mL of THF and 55 mL of hexane stirred at −20 °C (under Ar). The reaction mixture was stirred for 0.5 h at 0 °C and cooled to −70 °C, and Me_3SiCl (9.1 g, 83.2 mmol) was added. After 2.5 h, the reaction mixture was slowly warmed up to 0 °C and poured into 170 mL of water, and the product was extracted into ether. The combined organic extracts were washed with water and dried with K_2CO_3. Evaporation of the solvent and vacuum distillation of the product gave 13.7 g (80%) of imine **3**, b.p. 80—82 °C (8 Torr); n_D^{20} 1.4440. ^{1}H NMR, δ: 0.00 (s, 9 H, Me_3Si); 0.89 (t, 3 H, Me, *J* = 6.7 Hz); 1.17 (s, 9 H, Me_3C); 1.30 (m, 4 H, $H_2C(4)$, $H_2C(5)$); 1.55 (m, 2 H, $H_2C(3)$); 1.90 (m, 1 H, CHSi); 7.40 (d, 1 H, HC(1), *J* = 7 Hz).

(*E*)-2-(2-Benzyloxyethylidene)hexanal (5). A solution of imine **3** (8.6 g, 38 mmol) in 10 mL of THF was added over a period of 15 min to a freshly prepared solution of LDA (41.5 mmol) in 180 mL of THF and 40 mL of hexane stirred at −20 °C (under Ar). The reaction mixture was stirred for 40 min at −10 °C and cooled to −70 °C, and a solution of **4** (4.7 g, 31.4 mmol), prepared by a previously described procedure,[9] in 15 mL of THF was added dropwise over a period of 15 min. The mixture was stirred at the same temperature for 2.5 h, slowly warmed up to −20 °C, and diluted with 50 mL of water. The reaction mixture was acidified by addition of solid $(COOH)_2$ to pH 4, stirred for 40 min at ~20 °C, and poured into 120 mL of brine, and the product was extracted into $MeOBu^t$. The subsequent usual workup of the combined extracts gave 8.3 g of an oily product, whose chromatography on 90 g of SiO_2 (gradient elution: hexane→25% AcOEt in hexane) gave 4.0 g (55%) of **5** as a colorless oil, b.p. 115 °C (1.5 Torr). Found (%): C, 77.30; H, 8.63. $C_{15}H_{20}O_2$. Calculated (%): C, 77.55; H, 8.68. IR, ν/cm^{-1}: 3060—2860, 2740, 1690, 1640, 1500, 1470, 1450, 1380, 1340, 1320, 1230, 1180, 1090, 1080, 1030, 950, 910, 860, 700. ^{1}H NMR, δ: 0.90 (t, 3 H, Me, *J* = 7 Hz); 1.30 (m, 4 H, $H_2C(4)$, $H_2C(5)$); 2.20 (t, 2 H, $H_2C(3)$, *J* = 7 Hz); 4.37 (d, 2 H, $H_2C(8)$, *J* = 7 Hz); 4.60 (s, 2 H, $\mathrm{C\underline{H}_2Ph}$); 6.58 (t, 1 H, $H_2C(7)$, *J* = 7 Hz); 7.35 (m, 5 H, Ph); 9.40 (s, 1 H, $\mathrm{C(1)\underline{H}O}$). ^{13}C NMR,[*] δ: 14.0 (Me); 22.7 and 30.8 (CH_2); 24.25 (C(3)); 66.4 (C(8)); 73.05 (CH_2Ph); 144.2 (C(2)); 149.2 (C(7)); 193.7 (C(1)). MS, *m/z*: 203, 189, 145, 141, 132, 126, 107, 97, 95, 92, 91, 82, 78, 65, 57, 55.

(*E*)-2-(2-Benzyloxyethylidene)hexan-1-ol (6). $NaBH_4$ (1.99 g, 30 mmol) was added in portions to a solution of **5** (1.14 g, 8.58 mmol) in 90 mL of EtOH at 0 °C, and the suspension was stirred for 20 min at ~20 °C (TLC monitoring) and cooled to 0 °C; to decompose excess $NaBH_4$, 2.5 mL of AcOH was added. The reaction mixture was concentrated *in vacuo* to dryness, 50 mL of water was added to the residue, and the product was extracted into $MeOBu^t$. The usual workup of the extract gave 2.1 g of a reaction product, whose chromatography on 30 g of SiO_2 (gradient elution: hexane→20% Et_2O in hexane) gave 1.84 g (92%) of **6** as a colorless oil, b.p. 120 °C (1.5 Torr). Found (%): C, 76.44; H, 9.26. $C_{15}H_{22}O_2$. Calculated (%): C, 76.88; H, 9.46. IR, ν/cm^{-1}: 3600, 3550—3150, 3000—2860, 1670, 1600, 1490, 1470, 1450, 1380, 1360, 1320, 1230, 1120, 1070, 1030, 1000, 940, 850, 700. ^{1}H NMR, δ: 0.90 (t, 3 H, Me, *J* = 7 Hz); 1.35 (m, 4 H, $H_2C(4)$, $H_2C(5)$); 1.55 (m, 1 H, OH); 2.10 (t, 2 H, $H_2C(3)$, *J* = 7 Hz); 4.01 (d, 2 H, $H_2C(8)$, *J* = 7 Hz); 4.08 (s, 2 H, $H_2C(1)$); 4.50 (s, 2 H, $\mathrm{C\underline{H}_2Ph}$); 5.65 (t, 1 H, HC(7), *J* = 7 Hz); 7.30 (m, 5 H, Ph). 13C NMR (δ: 13.9 (Me); 22.9 and 31.0 (C(4), C(5)); 28.15 (C(3)); 66.0 (C(1)); 66.4 (C(7)); 72.4 ($\mathrm{\underline{C}H_2Ph}$); 121.8 (C(2)); 143.7 (C(7)). MS, *m/z*: 234 $[M]^+$, 203, 159, 148, 146, 143, 137, 127, 126, 125, 112, 110, 107, 106, 91, 85, 84, 69.

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[*] The ^{13}C NMR spectra of compounds **5—7** also contain signals of Ph groups at 128—138 ppm.

1-Benzyloxy-3-methylhept-2(*Z*)-ene (7). Py · SO_3 (Aldrich) (3 g, 18.9 mmol) was added in portions to a solution of **6** (2 g, 8.54 mmol) in 100 mL of THF stirred at 0 °C (under Ar). The mixture was stirred for 2 h at 0 °C (TLC monitoring) and cooled to −30 °C; a 0.8 *M* solution of $LiAlH_4$ in THF (96.2 mL, 76.9 mmol) was added dropwise, and the mixture was stirred for 0.5 h at −30 °C and for 20 h at −20 °C. Water (4 mL), 15% KOH (4 mL) and, finally, water (12 mL) were carefully added to the reaction mixture, the mixture was stirred for 10 min, and the precipitate was filtered off and thoroughly washed with $MeOBu^t$. The usual workup gave 2.2 g of a reaction product, whose chromatography on 40 g of SiO_2 (with hexane—ether (98 : 2) as the eluent) gave 1.21 g (65%) of **7** as a colorless oil, R_f 0.74 (A). Found (%): C, 82.20; H, 10.15. $C_{15}H_{22}O$. Calculated (%): C, 82.51; H, 10.16. IR, ν/cm^{-1}: 3000—2800, 1670, 1500, 1470—1450, 1380, 1360, 1340, 1310, 1240, 1200, 1130, 1090, 1075, 1030, 1010, 940, 730, 700. ^{1}H NMR, δ: 0.90 (t, 3 H, Me, *J* = 7 Hz); 1.32 (m, 4 H, $H_2C(5)$, $H_2C(6)$); 1.78 (s, 3 H, C(3)Me); 2.05 (t, 2 H, $H_2C(4)$, *J* = 7 Hz); 4.00 (d, 2 H, $H_2C(1)$); 4.50 (s, 2 H, $C\underline{H}_2Ph$); 5.40 (t, 1 H, HC(2), *J* = 7 Hz); 7.35 (m, 5 H, Ph). ^{13}C NMR, δ: 13.8 (Me); 22.5 and 30.2 (C(5), C(6)); 23.3 (C(3)$\underline{Me}$); 31.7 (C(4)); 66.1 (C(1)); 71.9 ($\underline{C}H_2Ph$); 121.3 (C(2)); 140.9 (C(3)). MS, *m/z*: 218 [M]$^+$, 217, 189, 176, 161, 160, 127, 108, 97, 91, 82, 71, 69, 68, 57, 55.

3-Methylhept-2(*Z*)-en-1-ol (8). Lithium (0.9 g, 128.1 mmol) was added in portions to a solution of **7** (1.62 g, 7.43 mmol) in 300 mL of liquid NH_3 stirred at −35 °C, the reaction mixture was stirred for 2.5 h at the same temperature, then NH_4Cl was added until the solution became colorless, and NH_3 was allowed to evaporate. Water was added to the residue and the product was extracted into ether. The usual workup of the extract gave 0.92 g of a reaction product, whose chromatography on 20 g of SiO_2 (gradient elution: hexane→15% ether in hexane) gave 0.77 g (81%) of **8** as a colorless oil, R_f 0.19 (B). Found (%): C, 74.25; H, 12.30. $C_8H_{16}O$. Calculated (%): C, 74.94; H, 12.58. IR, ν/cm^{-1}: 3600, 3580—3040, 3000—2800, 1660, 1380, 1340, 1240, 1160, 1100, 1060, 1000, 940, 840. ^{1}H NMR, δ: 0.90 (t, 3 H, Me, *J* = 7.2 Hz); 1.35 (m, 4 H, $H_2C(5)$, $H_2C(6)$); 1.73 (s, 3 H, C(3)Me); 2.06 (t, 2 H, $H_2C(4)$, *J* = 7.2 Hz); 4.10 (d, 2 H, $H_2C(1)$, *J* = 7 Hz); 5.40 (t, 1 H, HC(2), *J* = 7 Hz). ^{13}C NMR, δ: 14.1 (C(7)); 22.6, 30.5 (C(5), C(6)); 23.5 (C(3)$\underline{Me}$); 31.7 (C(4)); 59.0 (C(1)); 124.0 (C(2)); 140.4 (C(3)). MS, *m/z*: 128 [M]$^+$, 127, 109, 97, 96, 95, 82, 80, 71, 68, 67, 65.

3-Methylhept-2(*Z*)-enal (9) and its 2(*E*)-isomer. Manganese dioxide (10.3 g, 118.8 mmol), prepared by a previously described procedure,[10] was added to a solution of **8** (0.76 g, 5.94 mmol) in 120 mL of hexane stirred at −20 °C, and the mixture was stirred for 1 h (TLC monitoring). The precipitate was filtered off and thoroughly washed with hexane. The usual workup of the extract gave 0.56 g (75%) of a mixture of aldehydes 2(*Z*)-**9** and 2(*E*)-**9** in 9 : 1 ratio as a colorless oil, b.p. 184 °C. Found (%): C, 76.10; H, 11.00. $C_8H_{14}O$. Calculated (%): C, 76.15; H, 11.18. IR, ν/cm^{-1}: 3000—2800, 2740, 1670, 1630, 1470, 1450, 1400, 1380, 1230, 1185, 1145, 1080, 1010, 710. ^{1}H NMR, δ: 0.90 (t, 3 H, Me, *J* = 7 Hz); 1.40 (m, 4 H, $H_2C(5)$, $H_2C(6)$); 1.95 (s, 2.7 H, C(3)Me in *Z*-isomer); 2.17 (s, 0.3 H, C(3)Me in *E*-isomer); 2.20 (t, 0.2 H, $H_2C(4)$ in *E*-isomer, *J* = 7 Hz); 2.55 (t, 1.8 H, $H_2C(4)$ in *Z*-isomer, *J* = 7 Hz); 5.90 (d, 1 H, HC(2), *J* = 8.2 Hz); 9.95 (d, 0.9 H, CHO *Z*-isomer, *J* = 8.2 Hz); 10.00 (d, 0.1 H, CHO in *E*-isomer, *J* = 8.2 Hz). ^{13}C NMR, δ: 13.8 (Me); 19.4 (C(3)$\underline{Me}$ in *E*-isomer); 22.7, 30.9 (C(5), C(6)); 24.9 (C(3)$\underline{Me}$ in *Z*-isomer); 32.7 (C(4) in *Z*-isomer); 40.3 (C(4) *E*-isomer); 128.3 (C(2)); 164.7 (C(3)); 190.6 (CHO). MS, *m/z*: 126 [M]$^+$, 125, 110, 108, 97, 82, 71, 68, 56, 44.

3-Methylhept-2(*Z*)-enoic acid (1). A solution of the above-described mixture of 2(*Z*)-**9** and 2(*E*)-**9** (0.1 g, 0.79 mmol) in 1.5 mL of EtOH was added at −20 °C to a vigorously stirred solution of $AgNO_3$ (0.28 g, 1.66 mmol) in 1.5 mL of water; then 3.5 mL of 1 *N* NaOH was added over a period of 10 min and the mixture was stirred for 1.5 h (TLC monitoring). The precipitate was filtered off, thoroughly washed with water and acidified with 5% HCl to pH 4, and the product was extracted into $MeOBu^t$. The usual workup gave 0.1 g of an oily reaction product; according to ^{1}H NMR spectroscopy, it was a mixture of acid **1** and its 2(*E*)-isomer in 9 : 1 ratio. The mixture was chromatographed on 10 g of SiO_2 (gradient elution: hexane→15% ether in hexane) to give 60.3 mg (60%) of **1** and 6.7 mg (6%) of 2(*E*)-**1** as colorless oils. Acid **1**, R_f 0.50 (B). Found (%): C, 68.00; H, 9.98. $C_8H_{14}O_2$. Calculated (%): C, 67.58; H, 9.93. IR, ν/cm^{-1}: 3000—2815, 1695, 1650, 1470, 1460, 1450, 1420, 1380, 1295, 1265, 1220, 1170, 1110, 1030, 930, 870, 715. ^{1}H NMR, δ: 0.97 (t, 3 H, Me, *J* = 7 Hz); 1.36 (m, 4 H, $H_2C(5)$, $H_2C(6)$); 1.90 (s, 3 H, C(3)Me); 2.66 (t, 2 H, $H_2C(4)$, *J* = 7 Hz); 5.70 (s, 1 H, HC(2)); 11.50 (br.m, 1 H, COOH). ^{13}C NMR, δ: 13.9 (Me); 22.3, 29.6 (C(5), C(6)); 25.6 (C(3)$\underline{Me}$); 33.3 (C(4)); 115.5 (C(2)); 164.2 (C(3)); 172.0 (C(1)). MS, *m/z*: 142 [M]$^+$, 127, 125, 124, 112, 100, 97, 95, 82, 72, 69, 67, 57, 56, 54.

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